A THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL DEGRADATION OF SOME BROMINE CONTAINING COPOLYMERS

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PREFACE

The work described in this thesis was carried out by the author between October, 1975 and September, 1978 at the University of Glasgow, in the Physical Chemistry Department which is under the general supervision of Professor G. A. Sim.

I am indebted to the Science Research Council for the award of a grant during the tenure of which this work was carried out.

I should like to thank my supervisors, Professor N. Grassie and Dr. A. Scotney for their interest, advice and continual encouragement throughout the course of this work.

My thanks are also due to my colleagues in the Macromolecular Chemistry Group for invaluable assistance and helpful discussions, and to various members of the Departmental technical staff, in particular Mr. J. Gorman and Mr. G. McCulloch.

Finally, I thank my wife, Brenda, for her help in typing this thesis, and for her patience, understanding and support during the period of this work.

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SUMMARY

The recent increasing commercial interest in the flammability properties of polymeric materials brought about by relevant legislation has stimulated renewed research into the nature and quantity of volatiles produced during polymer pyrolysis. By influencing the degradation behaviour of a polymer in either a physical or chemical manner, its burning properties can be drastically altered.

The non-flammability properties of halogenated species has stimulated interest in their thermal stability both in the form of chemical additives and as an integral part of the polymer molecules. This work is aimed at increasing our understanding of the mechanisms involved in the thermal degradation of a brominated methacrylate monomer in a number of different copolymer and polymer blend environments.

A brief description of the various ways in which a fire-retardant may affect a burning polymer is presented in Chapter 1. This introductory chapter also reviews briefly the relationship between chemical structure and the thermal stability of vinyl polymers.

A list of the chemicals used and polymerisation conditions are given in Chapter 2 along with details of the apparatus and experimental techniques employed.

Two methods for obtaining compositions of copolymers of

2-bromoethyl methacrylate and methyl acrylate are described and evaluated in Chapter 3. Reactivity ratios for the monomer pair were calculated using a Nuclear Magnetic Resonance spectroscopy method.

In Chapter 4 the thermal properties of poly(2-bromoethyl methacrylate) homopolymer are found to be consistent with a depropagation mechanism giving monomer in yields greater than 90%. Trace amounts of ester decomposition products are formed at higher temperatures. This chapter also includes a detailed review of the thermal degradation mechanism of poly(methyl acrylate).

Chapter 5 presents a qualitative and quantitative study of the various degradation fractions from copolymers of 2-bromoethyl methacrylate and methyl acrylate covering the entire composition range. The presence of compounds such as methyl bromide, 1,2 dibromoethane and acetaldehyde provides evidence for interactions occurring between the two degrading monomer units.

A qualitative study on the thermal behaviour of 1:1 (by weight) blends of poly(2-bromoethyl methacrylate) and poly(methyl acrylate) is given in Chapter 6. This study provides evidence for an intermolecular reaction between the two polymers.

The results from Chapters 4, 5 and 6 are discussed in Chapter 7 in terms of possible mechanisms of formation of the various products of degradation in the 2-bromoethyl methacrylate - methyl acrylate copolymer system.

Qualitative studies on the thermal degradation of an approximately 1:1 copolymer of 2-bromoethyl methacrylate and styrene are presented in Chapter 8. The nature of the volatile products suggest that depropagation reactions predominate to give the respective monomers but that transfer processes involving hydrogen and bromine atoms on the ester group of a 2-bromoethyl methacrylate unit can also occur.

Chapter 9 describes the qualitative aspects of the thermal decomposition of an approximately 1:1 copolymer of 2-bromoethyl methacrylate and acrylonitrile. The methacrylate unit participates in the nitrile oligomerisation reaction with concomitant release of fragments from the ester group giving volatiles such as acetaldehyde and 1,2 dibromoethane. At higher temperatures these cyclic structures break down to give a number of volatile gases.

The results from all the copolymer systems are summarised in Chapter 10 which also includes suggestions for future work.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In recent years increasing concern about the condition of our living environment has brought with it relevant legislation designed to reverse the trend of deterioration. In this context the flammability properties of materials, especially synthetic organic polymers have become a major topic of research in both the commercial and academic fields. This has led to the development of a large number of compounds which retard the burning process. The chemistry of fire-retardants centres around six elements; phosphorous, antimony, chlorine, bromine, boron and nitrogen. Commercial fire retardants can be broadly divided into two general classes:-

a. those, in the form of additives, which are physically mixed with the polymer, usually during processing, to form a polymer/additive blend, for example, ammonium polyphosphate in rigid polyurethane foams.[1]

b. those which are incorporated into the macromolecular chain structure of the polymer during polymerisation. An example of this type is acrylic fibres made from various mixtures of

acrylonitrile, vinylidene chloride and vinyl bromide.[2]

The flame-retardant which may be present as an additive or as an integral part of the polymer chain may act in one of the following ways:-[3,4]

i. Forming a heat barrier by physically covering the polymer with a reflecting intumescent coating which reduces heat transfer from the heat source to the substrate and prevents low temperature degradation.

ii. Diluting the concentration of combustible gases by the production of inert species such as carbon dioxide and nitrogen.

iii. Producing a dust which acts as a heterogeneous catalyst in deactivating the radicals involved in flame propagation.

iv. Quenching the volatilisation process and increasing the proportion of char.

v. Altering the degradation and decomposition reactions to produce non-flammable volatiles (usually halogenated species).

This last effect is perhaps the most important of all the flame retardant mechanisms, because of the relatively small proportion of chemical flame-retardant required for a significant effect. Unlike inert gases, halogens or halogen derivatives strongly affect the flame velocity in concentrations of less than one per cent. The flame propagating cycle is thought to involve radical species such as H· and ·OH radicals and halogen compounds trap these radicals in the following way,

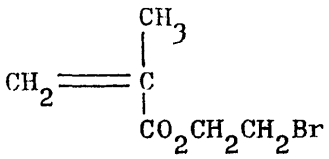
$$RX + H\bullet \longrightarrow HX + R\bullet$$

The R· radical is less reactive than the H· radical which it replaces so this substitution results in flame inhibition. The

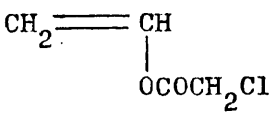
effectiveness of halogen compounds as flame-retardants is in the order I,Br > Cl ≫ F with bromine acting primarily in the flame zone while chlorine functions partially in slowing condensed phase reactions. Bromine is found to be twice as effective as chlorine on a weight basis or about four times on a mole basis. Hence, evolution of halogenated pyrolysis products removes heat from the flame reaction zone which in turn inhibits further combustion.

There are several distinct stages in the burning process itself[4,5]; heating, degradation and decomposition, volatilisation and oxidation. The flame feeds on the volatile pyrolysis products which are evolved in thermal degradation processes and it is the nature and amount of these volatiles which ultimately determine the flammability properties of the polymer sample.

This research is part of a larger programme being carried out at the University of Glasgow concerning the effect of a number of flame-retardant additives and comonomers on the thermal degradation behaviour of some common polymer systems. The work described in this thesis deals specifically with the thermal degradation of a number of copolymers containing various amounts of the brominated monomer, 2-bromoethyl methacrylate.



Other halogenated monomers which may be studied by later workers include chloro-vinyl acetate (A), para-bromostyrene (B), 2,3 dibromopropyl methacrylate (C) and 2,3 dibromopropyl acrylate (D).



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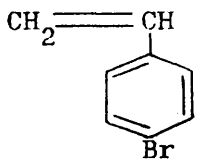

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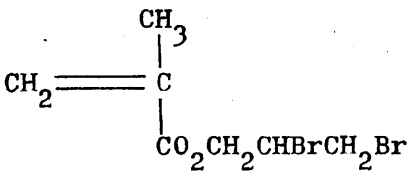

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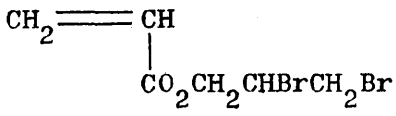


(D)

It is anticipated that studies of this kind may provide a better understanding of the chemistry and reaction mechanisms involved in existing commercial fire-retardant systems and contribute to a fund of information for assisting in the choice of notable fire-retarded polymer systems. Such studies should make it possible to determine the optimum conditions for maximum effectiveness of the fire-retardant with minimum loss of the physical properties of the parent polymer.

In order to study the primary chemical processes which take place during the thermal decomposition stage, degradations were carried out either under high vacuum conditions or in a dynamic inert atmosphere. These conditions assist in the removal of primary decomposition products, thus inhibiting secondary processes which can complicate the overall reaction and make it more difficult to identify the basic steps. If pyrolysis is carried out in air, there is the additional complication of oxidation reactions which can mask the pure thermal degradation mechanisms.

A general description of polymer degradation is included in order to relate the various features of thermal decomposition of the brominated copolymers to the known behaviour of polymers in general.

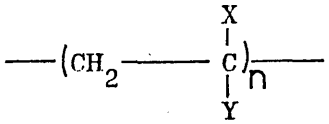
1.2 DEGRADATION OF POLYMERS

A polymer may 'degrade' when exposed to a variety of agencies which include the physical action of heat, light and mechanical stress or chemical influences such as oxidation hydrolysis etc. These agencies may act together or separately depending on fabrication conditions, environment and application of the polymeric material. Most research however, has involved the study of one of these variables under closely controlled conditions.

The information gained from thermal degradation studies are of particular importance from a practical point of view. It not only helps to explain the behaviour of polymers at elevated temperatures but possibly more important can help in the design and synthesis of new materials to meet new or existing requirements.

1.2.1 Classification of Reactions

The thermal degradation behaviar of vinyl polymers with the general formula,



can be classified into two distinct categories:-[6]

(a) Chain Scission or Depolymerisation Reactions

(b) Non-chain Scission or Substitution Reactions

Chain scission reactions are characterised by the breaking of the main polymer chain backbone, so that at any intermediate stage the products are similar to the starting material in the sense that monomer units are still distinguishable. New types of end groups may or may not appear depending on the nature of the chain scission process.

In non-chain scission reactions, the substituents attached to the main chain are involved in rearrangement and/or elimination processes so that the chemical nature of the repeat unit is altered although the chain structure may remain intact. Any volatiles produced from these reactions will be chemically unlike monomer.

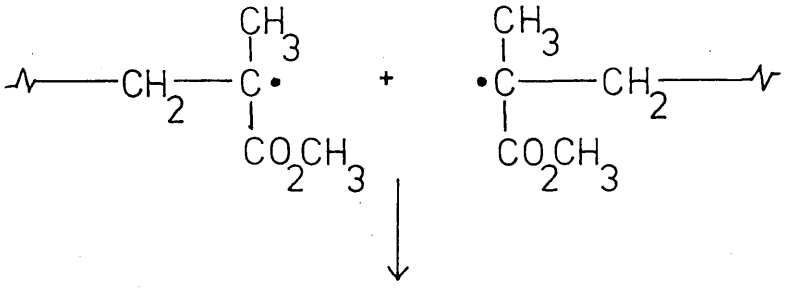
A polymer may undergo one or both reactions depending on its chemical nature, the temperature and the mode of initiation of degradation.

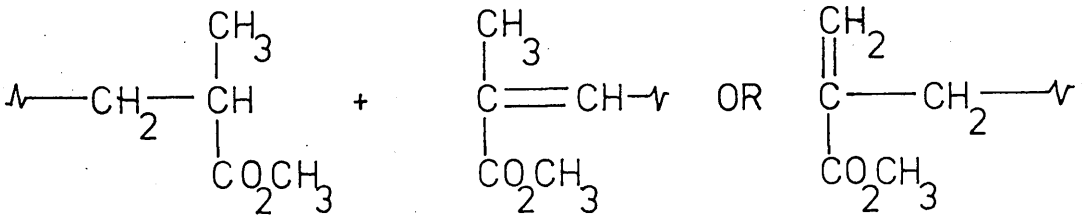
(a) Chain Scission or Depolymerisation

The classic example of a polymer which undergoes a chain scission or depolymerisation reaction is poly(methyl methacrylate) (PMMA). Monomer is the exclusive product of degradation in the 150-500^{o}C temperature range.[7]

Grassie and Melville studied changes in the molecular weight of PMMA residues after various extents of volatilisation under high vacuum conditions and concluded that the degradation process is the reverse of polymerisation. Polymeric free radicals are formed which subsequently 'unzip' to produce monomer. This interpretation seems reasonable since the addition of equimolar quantities of the radical scavenger 1,4 diaminoanthraquinone

completely inhibits the degradation reaction. However, monomer production occurs in two stages and the relative quantities formed at each stage is a function of the molecular weight of the polymer sample. Grassie and Vance[8] and more recently McCallum[9] have proposed that the unsaturated terminal units formed as a result of termination by disproportionation during polymerisation are the centres of initiation for the low temperature reaction occurring above 200°C.





At temperatures above 300°C the unzipping radicals are formed by random chain scission.

Other systems which depolymerise to produce monomer as the sole degradation product include poly(α-methyl styrene)(PαMS) and poly(tetrafluoroethylene)(PTFE). However, there are depolymerisation reactions which yield less than one per cent of monomer. Poly(ethylene)(PE) is such a system.[10,11]

The early studies of PE showed that the degradation products

consist of a continuous spectrum of hydrocarbon fragments. Oakes and Richards[12] found that initiation takes place at oxygenated structures which act as 'weak links' and propagation may proceed through points of branching. The degradation products from linear PE can be explained in terms of a random chain scission process followed by a series of inter-and intramolecular transfer reactions.

The probability of transfer and depropagation are roughly equal in poly(styrene)(PS)which gives 42% monomer, while transfer reactions dominate in the decomposition of poly(methyl acrylate) (PMA) which produces only trace amounts of monomer.

The following general reaction scheme, proposed by Simha, Wall and Blatz[13,14,15] represents all these kinds of depolymerisation processes, the rates of monomer to chain fragments being governed by the relative rate of depropagation and transfer. Intramolecular transfer is regarded as a special case of depropagation in which a stable volatile fragment larger than monomer is produced.

Random initiation	$M_n \longrightarrow P_j + P_{n-j}$
Terminal initiation	$M_n \longrightarrow P_{n-1} + P_1$
Depropagation	$P_i \longrightarrow P_{i-1} + M_1$
Transfer	$P_i + M_n \longrightarrow M_i + P_j + M_{n-j}$
Termination	$P_i + P_j \longrightarrow M_i + M_j$

n is the chain length of the starting material and M_i, M_j etc. and M_i, M_j etc. represent respectively 'dead' polymer molecules and long chain radicals, i, j etc. monomer units in length.

Effect of Polymer Structure on Depolymerisation

The relative importance of depropagation and transfer reactions depend upon polymer structure. For example, substitution of the tertiary hydrogen atom in polystyrene by deuterium results in an increase in the monomer yield from 42% to 70%.[16] Substitution by a methyl group completely suppresses transfer processes with P $\propto$ MS yeilding exclusively monomer. Methyl substitution on the aromatic ring or deuterium replacement of the β - hydrogen atoms has no effect. Hence, substitution of the $\propto$ - hydrogen atom which is the most reactive hydrogen atom in the molecule results in a reduction of the products originating from transfer processes.

In general therefore, the relative importance of depropagation and transfer depends on two factors, namely the reactivity of the degrading polymer radical and the availability of reactive atoms (usually hydrogen atoms) in the polymer structure. Consequently transfer is favoured by an active radical and is less likely to take place with a resonance stabilised or sterically hindered radical while high yields of monomers are produced from polymers devoid of tertiary hydrogen atoms.

(b) Non-Chain Scission or Substituent Reactions

Reactions involving the pendant groups attached to the main chain cannot be unified by a single reaction scheme since they depend entirely on the chemical nature of the functional group. These substituent reactions will occur in any given system only if they can be initiated at temperatures lower than those at which main chain bonds are broken. Thus, substituent

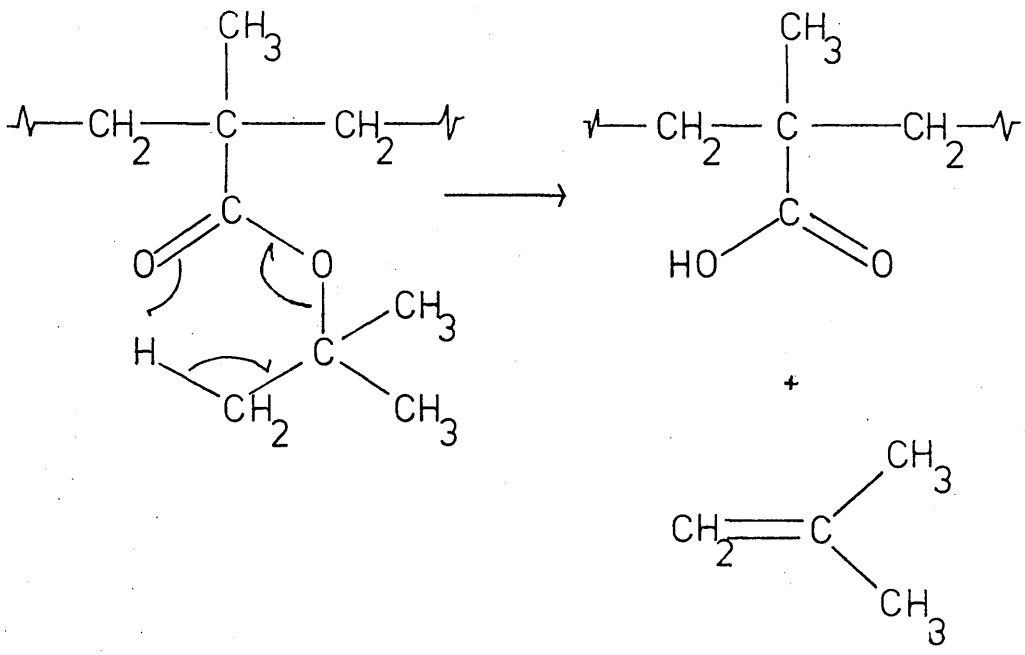
reactions are generally observed at relatively low temperatures and can be classified into three main types:-

(i) Ester decomposition reactions

(ii) Elimination reactions

(iii) Cyclisation reactions

Grant and Grassie[17] have shown that ester decomposition occurs during the thermal degradation of poly(tert-butylmethacrylate) forming isobutene and a residue of poly(methacrylic acid). The reaction takes place by a molecular mechanism facilitated by a six membered transition state involving the carbonyl group and a β-hydrogen on the alkyl group.

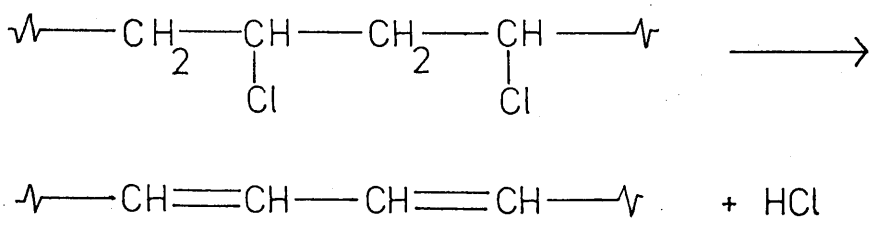


The relative importance of this reaction compared with depolymerisation depends upon the number of β-hydrogen atoms available for interaction and on the inductive effects of substituents on the alkyl group. Ester decomposition can also occur however at higher temperatures by a radical mechanism

involving the interaction of a polymer radical and a neighbouring pendant ester group.[18]

(i) Elimination Reactions

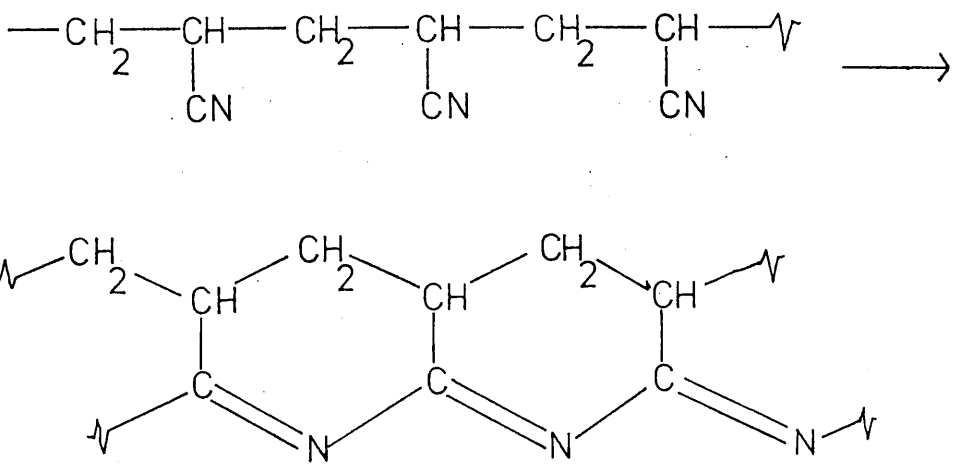
Poly(vinyl chloride) (PVC) eliminates HCl at temperatures below 300°C to produce a conjugated polyene chain,[19]



This reaction also occurs when the functional group is -OH, -Br or $-OCOCH_3$.[20]

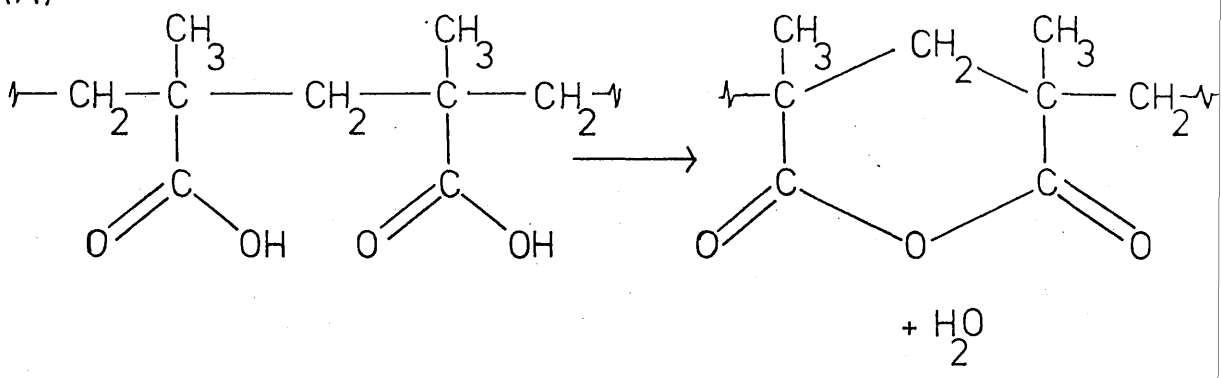
The actual mechanism by which HCl is eliminated from the polymer has been the subject of controversy for a number of years, although a radical mechanism appears to be favoured by most workers.[21,22,23]

(ii) Cyclisation reactions between adjacent pendant groups in the polymer chain give rise to a more stable structure which inhibits depolymerisation reactions. Poly(acrylonitrile) (PAN) undergoes such a reaction to produce a conjugated imine structure,[24] chemically different from the initial polymer without the evolution of small molecules,



In the thermal decomposition of poly(methacrylic acid)[25](A) and poly(methyl vinyl ketone)[26] (B) cyclisation occurs with concomitant production of water:-

(A)



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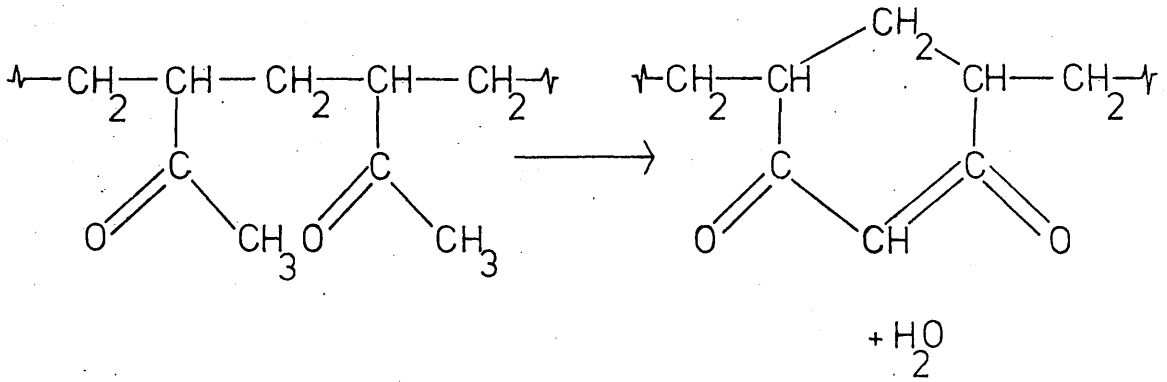


The mutual interaction of pendant groups may also occur intermolecularly, leading to a crosslinked network. Hence, the diversity of substituent reactions does not permit the formulation of a general reaction sequence. However, there are a number of features which are common to non-chain scission reactions:-

(i) All three types of substituent reactions lead to the formation of a structurally different polymer containing cyclic or conjugated

sequences or both as in PAN, which frequently lead to colouration of the residue.

(ii) Substituent reactions commence at temperatures below those at which depolymerisation normally occurs resulting in cyclic or crosslink structures which inhibit depropagation processes. Such behaviour is exemplified by poly(methacrylonitrile) in which cyclisation can occur at lower temperatures than monomer production.[27]

1.3 GENERAL CONSIDERATIONS

Although a great deal of information on the thermal stability of a polymer can be deduced from its chemical structure, other factors may influence the actual degradation behaviour. Such influences can arise from the mode and conditions of polymerisation and the subsequent history of the polymer sample. Though the concentration of abnormal or labile structures, built into the polymer during its formation, may be very low they can have a profound effect on the ultimate thermal stability of the sample, e.g. the unsaturated chain-ends can initiate depolymerisation in PMMA; small traces of copolymerised acid greatly affect the stability of poly(methacrylonitrile); and the dehydrochlorination reaction of PVC is believed to be initiated at structural abnormalities like chain branches or unsaturated structures.

Many 'model' reactions are converted to chain processes by the polymer environment. Thus, the loss of HCl from PVC occurs at temperatures some 200^{o}C lower than from low molecular weight chlorohydrocarbons. The results obtained from investigations of 'model' compounds therefore, cannot be expected to elucidate completely the mechanism of degradation of macromolecular analogues.

The thermal behaviour of copolymers and of polymer mixtures cannot necessarily be deduced by extrapolation from the processes occurring in the homopolymers. Copolymers of MMA and VC for example are less stable than either homopolymer, liberating methyl chloride at temperatures as low as 150°C.[28] Mixtures of the two homopolymers also leads to reduced stability of PMMA and the formation of products not obtained from either homopolymer degrading separately.[29] Hence, the degradation behaviour of a particular monomer type can be greatly influenced by the presence of a second monomer either in the same polymer chain or in the immediate environment. These interactions between degrading monomer units have been of particular interest in this present work. Such studies can not only provide data on the relative thermal stability and degradation behaviour of the particular copolymer system but can also afford valuable information on certain aspects of the degradation mechanisms of the respective homopolymers.

Most degradation reactions occurring in bulk polymer are believed to involve uncharged intermediates, occurring via radical or molecular pathways, since the charge on discrete ions cannot be delocalised by solvation and the dielectric constant of most molten polymers is too low to support charge separation. However, ionic or 'ion pair' intermediates may exist in solution degradation or in highly polar polymers.

1.4 AIM OF THIS WORK

This work will be concerned with the thermal degradation behaviour of a brominated methacrylate monomer in a number of

different copolymer and polymer blend environments. A qualitative and in some cases quantitative study of the main products of degradation will be carried out in order to determine the nature and extent of any interactions which may occur between the comonomer units or between the mixed polymers. These studies will ultimately lead not only to an understanding of the mechanism of degradation of the various copolymers and blends but also provide useful information on the respective homopolymer decomposition mechanism. It is anticipated that information of this kind will be relevant to the use of bromine containing compounds in fire-retardant polymer compositions.

CHAPTER 2

EXPERIMENTAL

This chapter will include information on monomer synthesis and purification as well as a description of the experimental techniques employed.

2.1 PREPARATIVE METHODS

Methyl methacrylate (MMA) (Hopkin and Williams Ltd.), styrene (S) (BP Chemicals International Ltd.) and methyl acrylate (MA) (BDH Chemicals Ltd.) were purified by drying over calcium hydride to remove water. The monomers were then distilled twice under vacuum, the first and last fractions being discarded.

Acrylonitrile (AN) (Hopkin and Williams Ltd.) monomer contained no inhibitor as dissolved oxygen acts as an effective inhibitor of polymerisation. The monomer was dried over calcium chloride before distillation twice under vacuum.

2-Bromoethyl methacrylate (2BEM) (Polysciences Ltd.) was purified by distillation under reduced pressure ($50^{o}C$ at 0.1 torr) using hydroquinone as inhibitor. The inital fraction was discarded to ensurecomplete exclusion of impurities.

2-Bromoethyl acrylate (2BEA) monomer was synthesised by esterification of acrylyl chloride with 2-bromoethanol.

Method:-

0.336 moles of acrylyl chloride (5% excess) was dropped slowly into a stirred mixture of 0.32 moles of 2-bromoethanol and 0.32 moles of N,N-dimethyl aniline. The mixture was refluxed for 24 hours. The fraction which distilled at 50-51°C at a pressure of 2.5 torr was then treated with K_2CO_3 to remove methacrylic acid impuriy. A further distillation was then carried out using hydroquinone as inhibitor, the distillate being characterised by infra-red as well as nuclear magnetic resonance spectroscopic analysis. When not in use, all monomers were stored at -18°C in the dark.

Purification of Initiator

Azobisisobutyronitrile (Eastman Kodak) was used as initiator (0.1% w/v) for all polymerisations. A solution in hot ethanol was filtered to remove insolubles, which are polymeric materials derived from decomposition of the initiator.[30] After cooling, the crystals were filtered off and dried under vacuum. The required weight of initiator was added to the dilatometer as a fine powder.

Purification of Solvents

Methyl Acetate (BDH Chemicals Ltd.) and Toluene (Hopkin and Williams) were dried over calcium hydride for between two and four days prior to use. The solvents were then distilled twice

under vacuum, the middle fraction being used in each case.

2.2 POLYMERISATION AND PURIFICATION TECHNIQUES

All homopolymers and copolymers were prepared by free radical initiation, the polymerisations being carried out in Pyrex glass dilatometers with 10ml graduated stems. The liquid monomers and solvents were degassed four times under vacuum before distillation from a graduated reservoir into the dilatometer containing the required weight of initiator. The dilatometer was then sealed off under a vacuum better than 10^{-5}torr. All polymerisations were carried out in a thermostat at $60 \pm 0.02^{\circ}C$. The extent of polymerisation was restricted to 10% for homopolymers and 5% for copolymers by monitoring the volume contraction on the calibrated stem of the dilatometer. Once the required conversion had been attained, the contents were poured slowly into a large volume (about twenty times the reaction volume) of non-solvent. The precipitated polymers were then redissolved, reprecipitated and dried to ensure complete removal of solvent. The polymers were finally dried in vacuo at $60^{\circ}C$ for between two and four days. Table 2.1 summarises the polymerisation conditions for the homopolymer systems studied.

Homopolymer	Polymerisation Solvent	Degree of Conversion	$\bar{M}_n \times 10^3$
P2BEM	Methyl Acetate	12%	3.33
PMMA	Bulk	11%	3.42
P2BEA	Methyl Acetate	-	-
PMA	Methyl Acetate	8%	6.17
PS	Bulk	10%	1.56

Table 2.1 Details of Homopolymer Polymerisations

The conversion of P2BEA was considerably beyond 10%. The polymer formed a gel in the methyl acetate, which formed a white solid on addition of non-solvent. The polymer could not be completely dissolved, due probably to crosslinking, and was therefore not reprecipitated.

2.3 COPOLYMERISATION

Monomer Feed Ratios

The molar ratios of monomers necessary to produce copolymers of the desired composition were calculated using the copolymer composition equation[31,32,33,34]

$$\frac{d(m_1)}{d(m_2)} = \frac{P_1}{P_2} = \frac{M_1}{M_2}\,\frac{(r_1 M_1 + M_2)}{(M_1 + r_2 M_2)}$$

where P_1/P_2 is the ratio of molar concentrations of the monomers in the copolymer, and M_1/M_2 is the molar ratio of the monomers in the feed. This relationship applies if the extent of polymerisation is sufficiently low for the monomer concentrations in the feed to remain unchanged. r_1 and r_2 are the reactivity ratios of the two monomers.

In the present work four copolymer systems were studied, namely:- 2BEM-MA (A), 2BEM-MMA (B), 2BEM-S (C) and 2BEM-AN (D). Table 2.2 summarises the polymerisation conditions employed in the synthesis of these systems:-

Table 2.2 Polymerisation Details of Copolymer Systems

Copolymer System	Polymerisation Medium	Solvent	Temperature	Degree of Conversion	$\bar{M}n$
A (1-4)	Solution	Methyl Acetate	60°C	4-9%	Variable
B	Solution	Methyl Acetate	60°C	9%	-
C	Solution	Toluene	60°C	4%	109,000
D	Bulk	-	60°C	10%	-

Reactivity ratios of the system 2BEM-S are available[35] as follows: r_1(2BEM) = 0.44 ± 0.02, r_2(S) = 0.35 ± 0.02 and reactivity ratios for the system 2BEM-MA were determined by a method outlined in the following chapter. Ractivity ratios for the other two systems were not available but copolymers of the appropriate composition required were made using reactivity ratios of related systems. Subsequent analysis of these copolymers indicated the validity of these assumptions. Only one copolymer was studied in each of the systems B, C and D.

2.4 THERMAL ANALYSIS TECHNIQUES

(a) Thermal Volatilisation Analysis (TVA)

This technique is now well established in thermal degradation analysis and is very well documented in a series of publications by McNeill.[36,37] It may be useful, however, to discuss briefly the general aspects and practical details employed in this work.

TVA involves the continuous measurement of the pressure exerted by volatile products evolved from the polymer sample, as it is heated through a linear temperature programme, usually 10^{o}/min. Degradation is carried out under high vacuum, the volatiles being continuously pumped from the heated sample.

Differential condensation TVA[38,39] involves a number of cold traps at various temperatures in a geometrically equivalent parallel arrangement as in Figure 2.1.

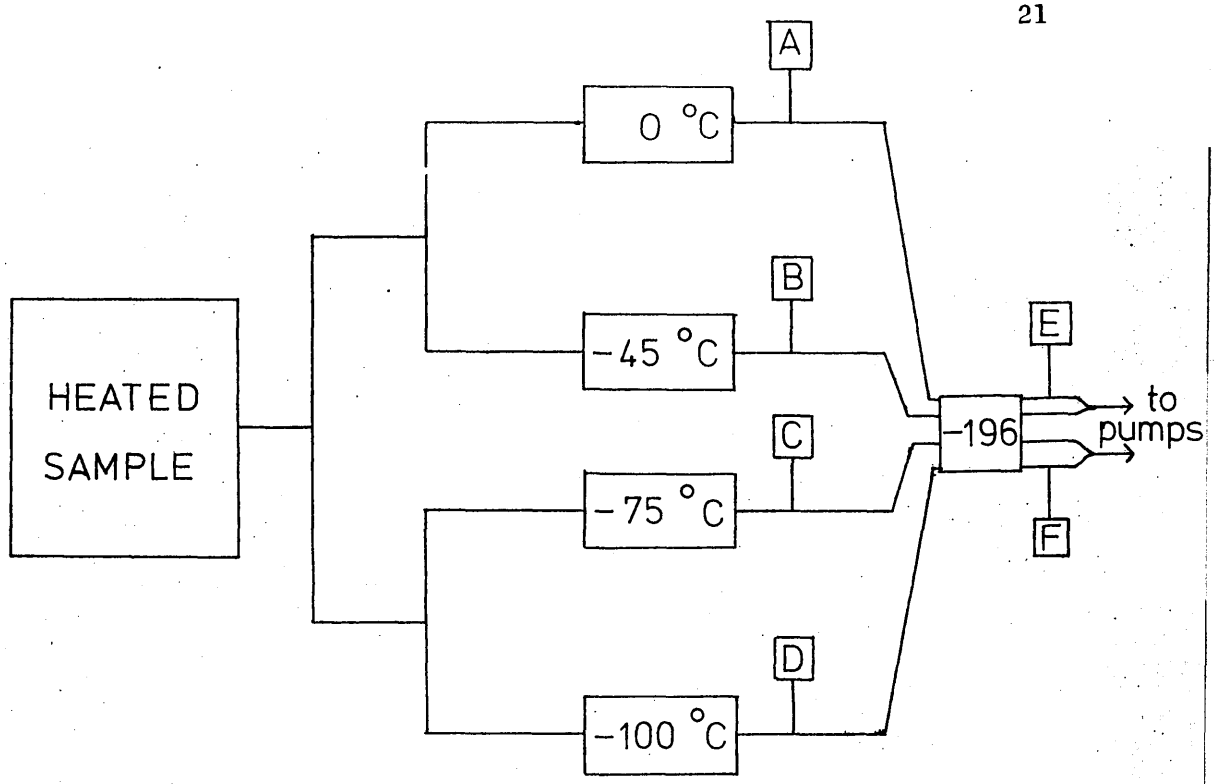


Figure 2.1 Schematic Representation of Differential Condensation TVA

Pirani gauges A, B, C and D positioned behind each cold trap give a measure, which is non-linear, of volatiles which pass through the respective cold trap. Pirani E records the response due to non-condensable gases.
The volatile products are distributed evenly among the four limbs of the TVA apparatus.
The oven temperature, together with the outputs from each of the Piranis are displayed on a multipoint recorder.
The thermogram produced, therefore, is a record of the rate of volatilisation of the polymer sample as a function of temperature. It also gives a preliminary impression of

the relative distribution of condensable products from thermal degradation on the basis of their condensability. The products of degradation may be divided into two main catagories:-

(a) the involatile residue,

(b) the volatile products, which may be further subdivided into three classes:-

(i) those products volatile at degradation temperatures but involatile at ambient temperatures (Cold Ring Fraction)

(ii) products volatile at degradation tempratures but involatile at the tempratures of the various cold traps $0^{o}C$, $-45^{o}C$, $-75^{o}C$, $-100^{o}C$ and $-196^{o}C$ (Condensables)

(iii) products volatile, even at liquid nitrogen temperatures (Non Condensables).

The involatile residue which remains on the base of the TVA tube may be analysed by infra-red spectroscopy. The cold ring fraction formed at the top of the degradation tube, cooled by a water jacket, and which is not therefore recorded by the Pirani gauges, can be investigated by dissolution of this fraction with an appropriate solvent. A few drops of the solvent are gently rolled around the top of the tube and the resulting solution poured into a suitable container for analysis by NMR or infra-red spectroscopy. If this fraction is solid, then samples for analysis may be obtained by scraping the sides of the tube

with a spatula.

Condensable products may be analysed by on-line distillation into appropriate receivers for infra-red spectroscopy, mass spectrometry or gas-liquid chromatographic analysis.

The non-condensable products are lost in this continuously pumped method, but may be collected for identification by employing a closed system technique described by McNeill and Neil.[40]

Operating Conditions

The heat source was a modified Perkin Elmer F11 oven equipped with a linear temperature programmer by which a sample can be heated isothermally or linearly from ambient temperature up to 500°C at heating rates from 1 to 40°/min. All TVA thermograms employed a heating rate of 10°/min.

The oven temperature is recorded using a chromel-alumel thermocouple fixed externally at the base of the TVA tube. The difference in temperature between the oven temperature and that of the sample is a function of temperature but decreases with increasing temperature as shown in figure 2.2. The sample temperature may be known by insertion of a second thermocouple on the inside of the tube base.

A small bead of Apiezon 'L' grease is used to improve thermal contact between metal and glass, and to stimulate molten polymer.

All homopolymers were degraded as 50mg powdered samples.

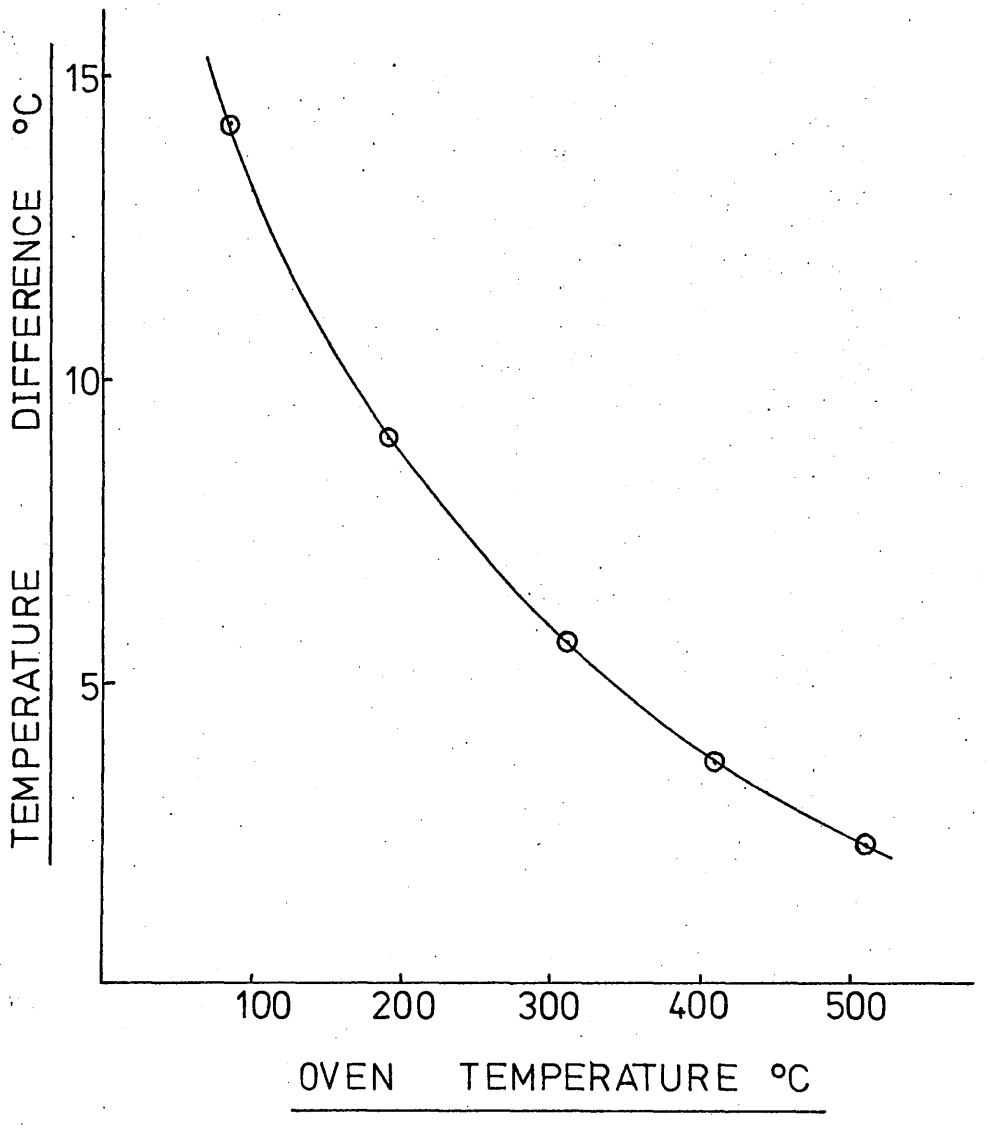


FIGURE 2.2 TVA TEMPERATURE CALIBRATION PLOT

Blends

Polymer blends were degraded as thin films. Both homopolymers were dissolved in acetone to a concentration of 30mg/ml. The two solutions were then thoroughly mixed and the solvent removed under vacuum, leaving a thin film of the blend on the base of the TVA tube. The sample was then heated isothermally at 120°C for one hour to ensure complete removal of solvent. Films cast from such solutions are opaque, as a result of the different refractive indices of the two polymer phases. The polymers are said to be incompatible and during pyrolysis interaction of the two components can take place only at phase boundaries or by diffusion of small molecule products from one phase into another.

The temperatures of the cold traps used in all TVA experiments were 0°C, -45°C, -75°C and -100°C.

All degradations were carried out in a tube measuring 20cm in length with a base area of 12cm^2.

Subambient TVA

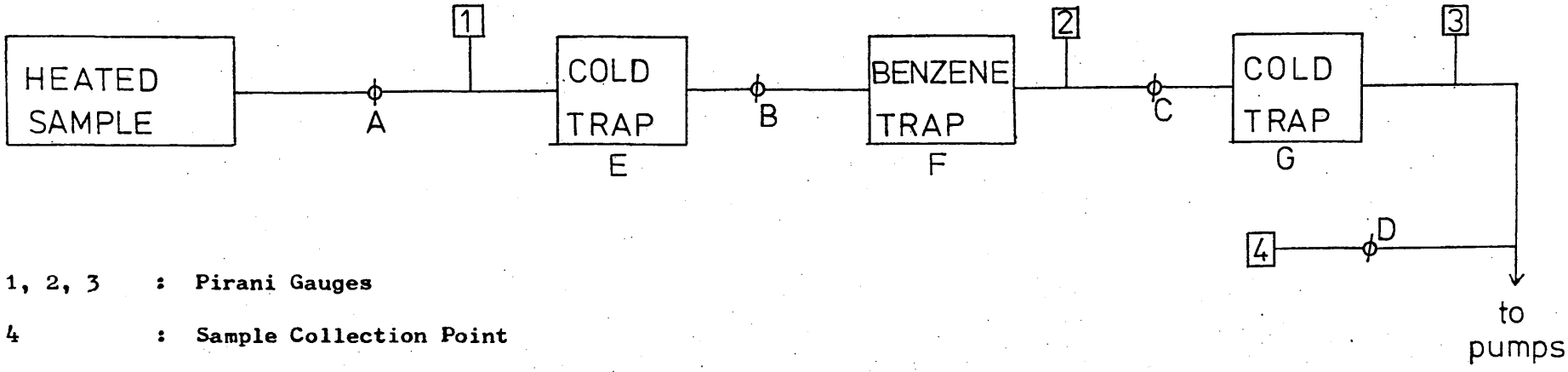
At the end of a TVA experiment, the various volatile products of degradation of the sample, except for gases not condensable at -196°C, are condensed in the cold traps in the TVA system, from which they are removed for analysis. The possibility of dividing the products into fractions according to volatility has led to the development of a system known as subambient TVA,[41] adapted from work by Ackerman and McGill.[42] The technique is based on the principle

that when a frozen mixture of different compounds is allowed to warm slowly, under high vacuum conditions and with continuous pumping, fractionation occurs as the separate components of the mixture distill at different rates, dependent on temperature. Therefore, TVA followed by subambient distillation of condensable products is a technique employed to isolate and identify individual products from degradation, on the basis of their volatility. The apparatus is described schematically in Figure 2.3.

As this technique has been used extensively in this present work it is pertinent to outline the procedure in some detail.

Thermal degradation is carried out in the usual fashion under continuous pumping conditions using the same apparatus described for basic TVA, the condensable products being trapped in the first U tube cold trap, E. The bottom 5cm of the jacket liquid is then surrounded by liquid nitrogen until the thermocouple indicates that the bottom of the tube has reached -196^{o}C, this creates a temperature gradient within the cold finger tube. Tap C is then closed and the products from the degradation experiment are allowed to distill into tube T (Figure 2.4). Gradually the liquid nitrogen level surrounding the benzene trap is raised until all the volatiles have condensed in tube T, the pressure being monitored by Pirani 2.

When no residual pressure is being measured and the benzene



1, 2, 3 : Pirani Gauges

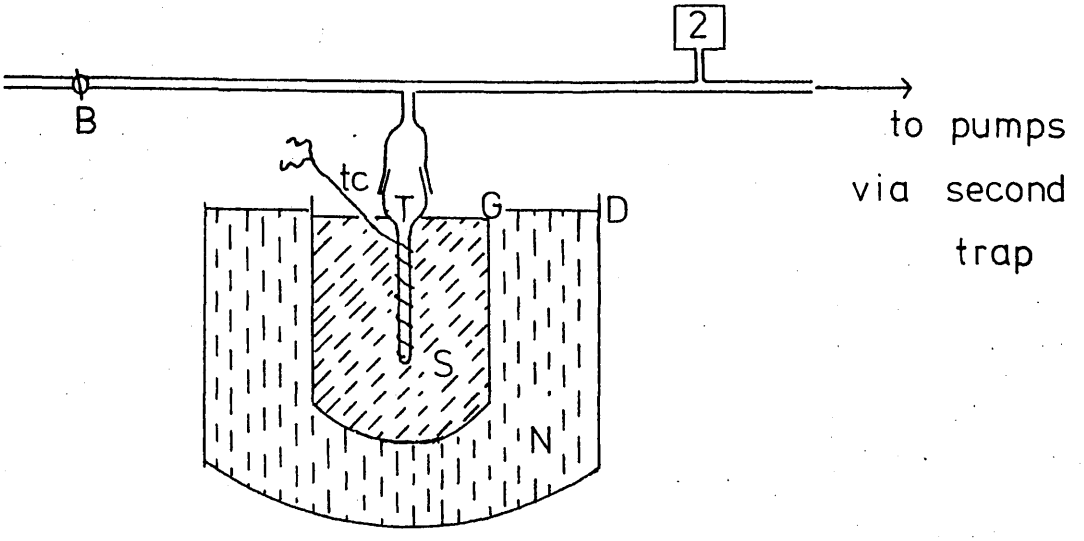
4 : Sample Collection Point

A, B, C, D : Stopcocks

E, G : U Tubes

F : Benzene Trap

FIGURE 2.3 SCHEMATIC DIAGRAM OF SUB-AMBIENT TVA.



2 : Pirani Gauge 2
T : Sample Tube (with B34 joint)
tc : Chromel Alumel Thermocouple Leads
S : Benzene (or para-Xylene)
N : Liquid Nitrogen
D : Dewar Flask
G : Pyrex Glass Round Bottomed Tube
B : Stopcock B

FIGURE 2.4 DETAIL OF BENZENE TRAP

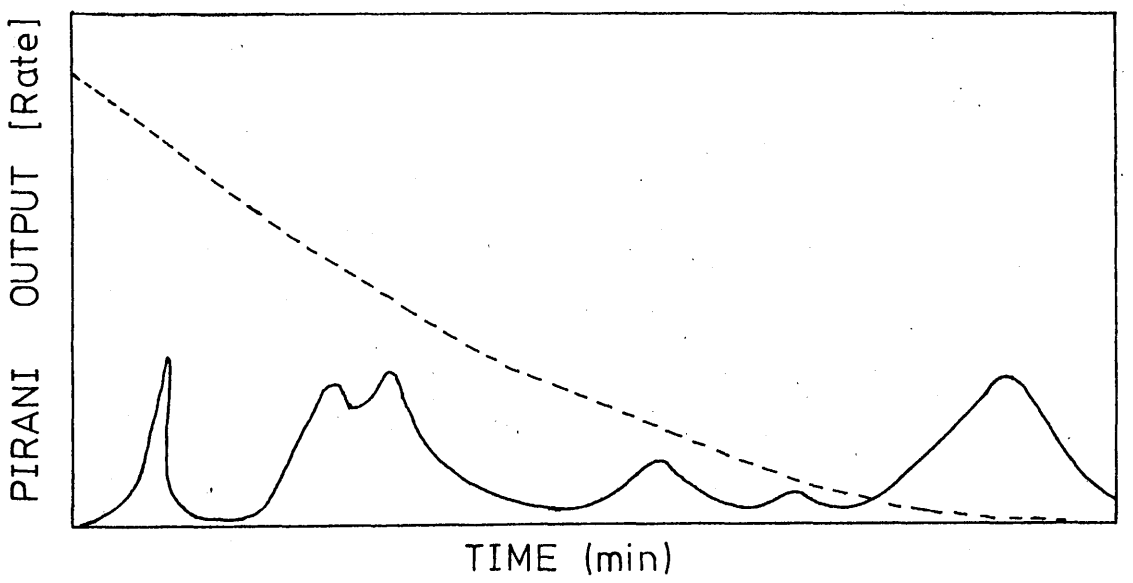


FIGURE 2.5 TYPICAL SUBAMBIENT TVA TRACE

trap is totally frozen, tap A is closed and tap C opened to the pumps. The outer liquid nitrogen trap is then removed and the products allowed to distill into the second U tube trap cooled to -196°C. As each product distills, Pirani 2 measures a change in pressure which is displayed as a series of peaks on a recorder. A typical trace is shown in Figure 2.5. Although a linear heating rate is not achieved (Figure 2.5) this rate is reproducible over a large number of experiments if the same procedure is adhered to.

The distillation may be halted at any point merely by closure of tap C and replacement of the liquid nitrogen reservoir around the benzene trap. In this way single products may be isolated and distilled into an appropriate receiver for qualitative as well as quantitative analysis. This initial separation therefore, makes identification of all condensable degradation products easier and reduces the possibility of masking certain minor products. As this technique depends solely on the volatility of condensable products under operating vacuum conditions, separation is by no means complete being a function of rate of warm up, quantity of product and the physical characteristics of the apparatus.

The main value of the technique in the present work was its ability to isolate methyl bromide from the mixture of condensable products, allowing quantitative estimation

by infra-red spectoscopy.

(b) Thermogravimetric Analysis (TGA)

TG curves were obtained using a Du Pont 950 thermo-balance. The boat-shaped plantinum sample holder measured 1 x 0.5 x 0.25 cm and the temperature measuring thermocouple was placed 0.1 cm from the powdered sample. A flow of nitrogen gas (80ml/min) was maintained throughout the degradation. Powdered samples of between 5 - 10 mgs were heated at 10^{o}/min to 500^{o}C. Weight loss data obtained by this method could be correlated with volatilisation information obtained from TVA, although the two techniques are not strictly comparable.

(c) Differential Thermal Analysis (DTA)

A Dupont 900 instrument was used to obtain DTA curves. Two identical tubes 25mm long and 4mm in diameter were placed in a heating block. The reference tube was packed with small glass beads and the sample tube with approximately 10mg of powdered polymer, each with a thermocouple. An atmosphere of nitrogen was maintained at a flow rate of 80cc/min. Heating was at 10^{o}/min to a temperature of 500^{o}C.

(d) Differential Scanning Calorimetry (DSC)

This technique measures the differential energy required to maintain a sample and inert reference at the same temperature throughout a programmed heating sequence. The area under the curve can, therefore, be equated to the heat of reaction by suitable calibration of the DSC cell. A Du pont 900 Thermal Analyser was used to obtain DSC curves.

Powdered samples of about 5 mgs were placed in open aluminimum pans $\sim 7mm^2$ which were placed on a heating block with a reference pan. An inert atmosphere was maintained by passing nitrogen gas over the sample at a rate of 80cc/min. Heats of reaction may be calculated using In, Sn, Bi and Zn as calibration metals with known heats of fusion, to determine the calibration co-efficient.

$$E \qquad \text{Where } E = \frac{\Delta H \, Wa}{A \quad Ts \quad Ts}$$

ΔH - Latent heat of fusion

W - Weight of sample (mg)

a - Heating rate (^{o}C/min).

A - Area under curve

Ts - Y axis scale (^{o}C/inch)

Ts - X axis scale (^{o}C/inch)

Table 2.3 DSC Cell Calibration

Metal	MPt ^{o}C*	Δ H cal/g*	E
In	156	6.8	146
Sn	232	14.4	153
Bi	271	12.0	165
Zn	419	24.4	178

*Handbook of Chemistry and Physics 54th Edition 1973-74.

2.5 ANALYSIS OF DEGRADATION PRODUCTS

Most spectra were recorded on a Perkin Elmer 257 spectrophotometer. Polymer samples were examined either in the form of a Kbr disc, in solution using NaCl cells, or as films cast on NaCl plates. Cold ring fractions were run

in solution using chloroform or carbon tetrachloride as solvent.

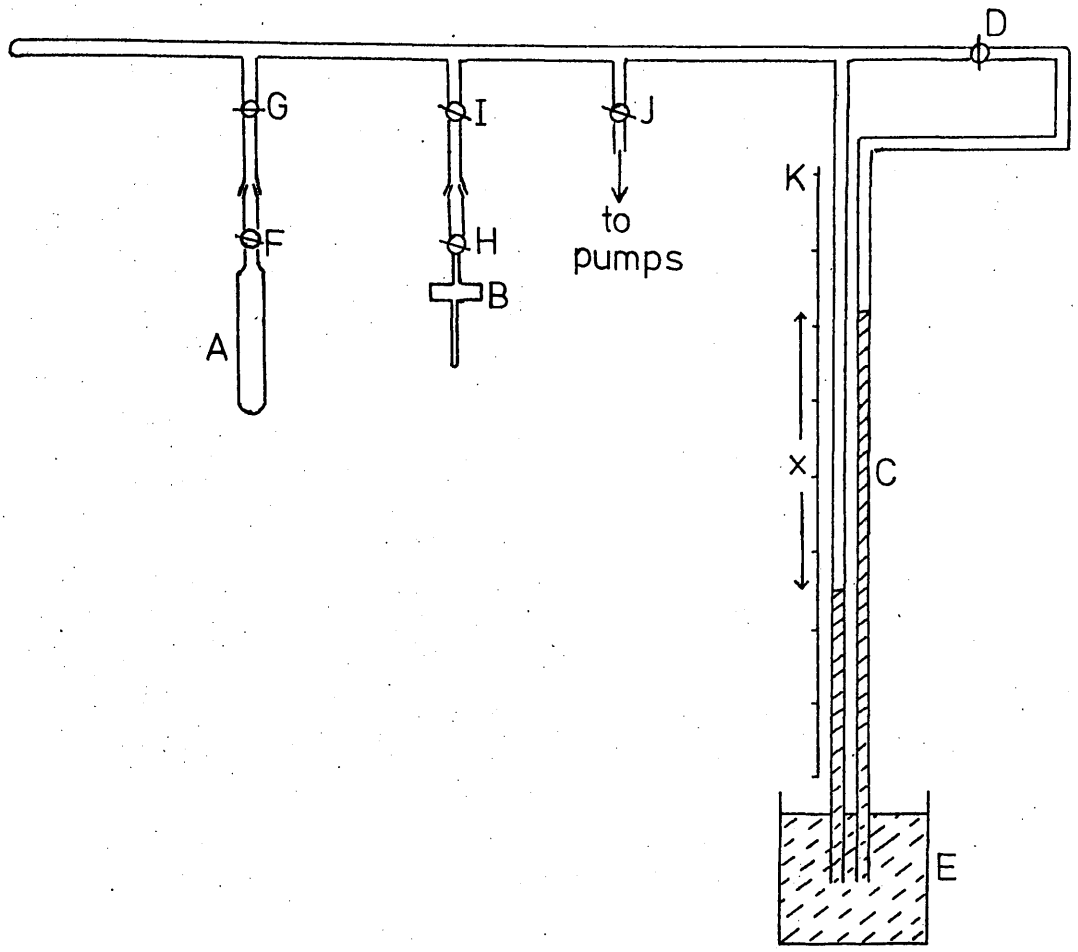
Volatile products were recorded as liquids between salt plates or in the gas phase using small gas cells with NaCl windows placed 4cm apart. For the examination of absorptions below $625cm^{-1}$, a Perkin Elmer 580 spectrophotometer was used. Solution spectra were then run using KBr cells.

Quantitative Infra-red Measurement of Gases

Some gaseous degradation products were measured quantitatively using the apparatus described in Figure 2.6. This method involves calibrating a gas cell of known volume by plotting the optical density of a particular absorption peak against pressure of reference gas in mmHg. The product from degradation may be isolated by subambient TVA and from optical density measurements can be related to a known pressure. At low pressures the gas may be treated as "ideal" and the equation $PV = nRT$ may be applied. Hence, the pressure of gas may be related to the number of moles of gas present and hence the weight, if the volume and absolute temperature are known.

The volume of the gas cell may be found by filling the gas cell with a suitable liquid from a burette. The temperature was assumed to be $290^{o}K$.

Reservoir A containing the reference gas is connected to the vacuum line and pumped to a pressure of 10^{-4}torr. All taps except F are opened to the pumps. Taps J and D are then closed and the pure gas introduced into the closed system by



A : Reference Gas Reservoir

B : Infra-red Gas Cell

C : Mercury Filled Manometer Tubes of Same Bore

X : Pressure of Gas (cm Hg)

K : Calibrated Scale

E : Mercury Reservoir

G, F, I, H, J, D : Stopcocks

FIGURE 2.6 APPARATUS EMPLOYED FOR CALIBRATION OF GAS CELL

opening tap F slowly and monitoring the drop in mercury level. The pressure due to the reference gas is then the difference in the mercury levels (X). Taps I and J are then closed and the infra-red spectrum taken. The rest of the system except the reservoir is then opened to the pumps. The gas cell is then reintroduced to the vacuum line and evacuated to tap H. The procedure can then be followed once again, by allowing the gas in cell B to expand into a larger volume, giving a lower pressure reading. In this way, graphs of optical density of particular peaks measured as peak heights versus pressure of gas were obtained.

For carbon dioxide calibrations, the infra-red detectors were flushed with nitrogen at a rate of 100cc/min from ten minutes before and during analysis, in order to completely exclude this gas from the reference beam.

Calibration plots were obtained for methyl bromide using the peak at ($1316cm^{-1}$) and carbon dioxide ($2344cm^{-1}$) as shown in Figure 2.7.

Mass Spectrometry

This was carried out on condensable or non-condensable products by direct expansion of these products into an AEI MS 12 mass spectrometer.

Gas-liquid Chromotography (GLC)

Two instruments were used during the course of this work, a Perkin Elmer F11 GC equipped with a hot wire detector and a Microtek GC 2000R with a flame ionization analyser. Quantitative measurement of liquid products was obtained by the addition of a known weight of suitable material as standard to a weighed quantity of liquid products. A/.....

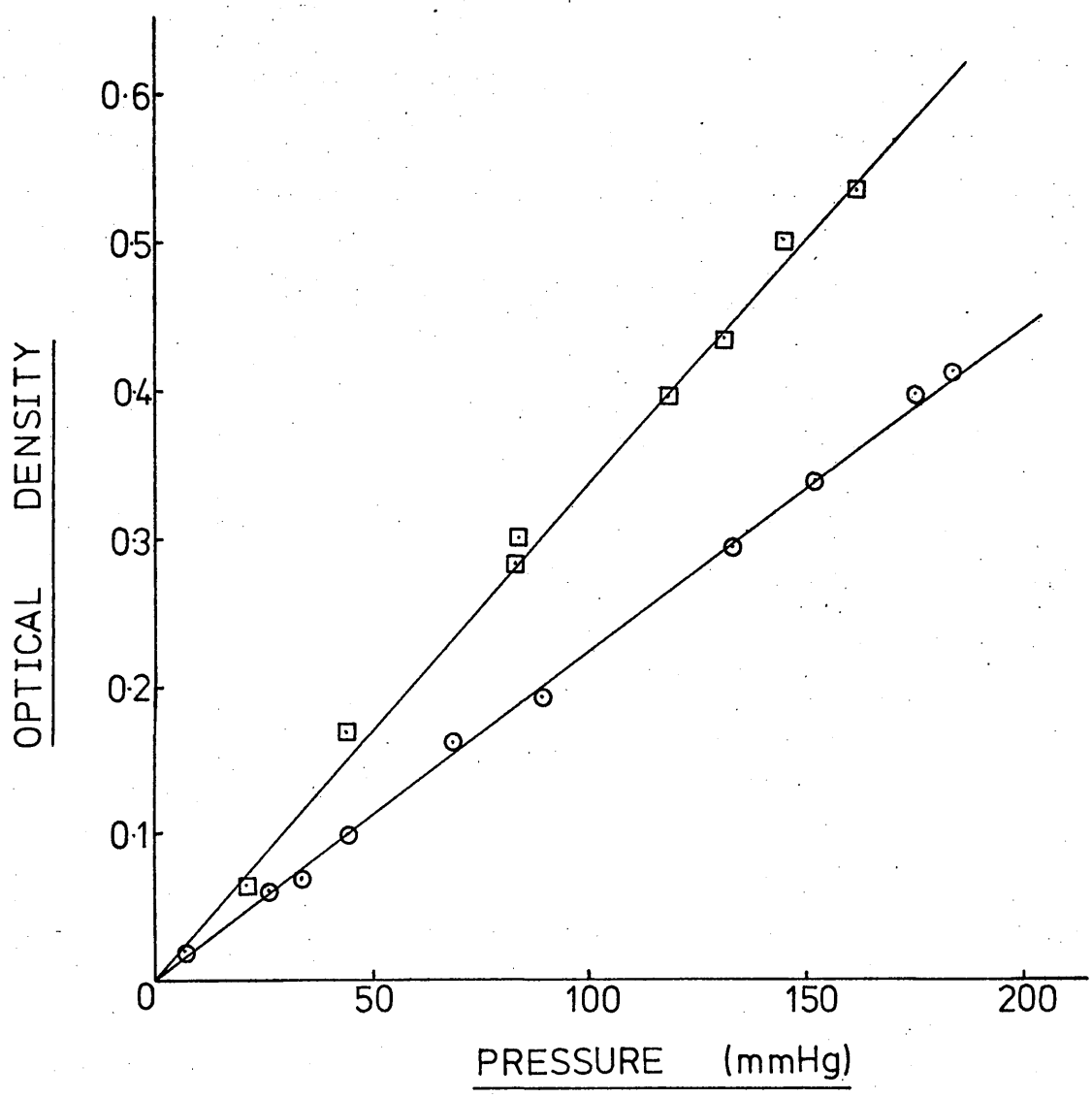


FIGURE 2.7 CALIBRATION PLOT FOR

CH_3Br ⊡ ($1316cm^{-1}$) and CO_2 ⊙ ($2344cm^{-1}$)

series of pure samples of each of the products were mixed with known amounts of the standard and run on the chromatograph to determine the sensitivity factor (K) of the product relative to the standard. Measurement of peak areas on glc traces was carried out using an Infotronic 309 Digital Processor, giving integral values for individual peak areas.

The sensitivity factor K is defined as:-

$$K_{P_1} = \frac{W_{P_1} I_R}{W_R I_{P_1}}$$

where W_{P_1} - Weight of Product

I_R - Integral of Reference

W_R - Weight of Reference

I_{P_1} - Integral of Product

and is determined graphically from a series of mixtures of known weights as illustrated in Figure 2.8.

For the series of 2BEM/MA copolymers n-hexyl acrylate was used as standard, whereas n-butanol was used as standard for P2BEA homopolymer.

Table 2.4 lists the sensitivity factors found for the various products of degradation of the copolymer system 2BEM-MA with n-hexyl acrylate as reference.

Table 2.4 Sensitivity Factors (K) of Products Using n-hexyl acrylate as reference.

Sensitivity Factor K	0.96	1.6	0.92	0.85	0.92	1.78	0.98	1.02
Product	2BEM	12DBE	MMA	MA	MeOH	CH_3CHO	EMA	2BE

The columns used for studying this copolymer system were 2 metre ⅛" od 15% LB - 550X on chromosorb W80-100 mesh as supplied

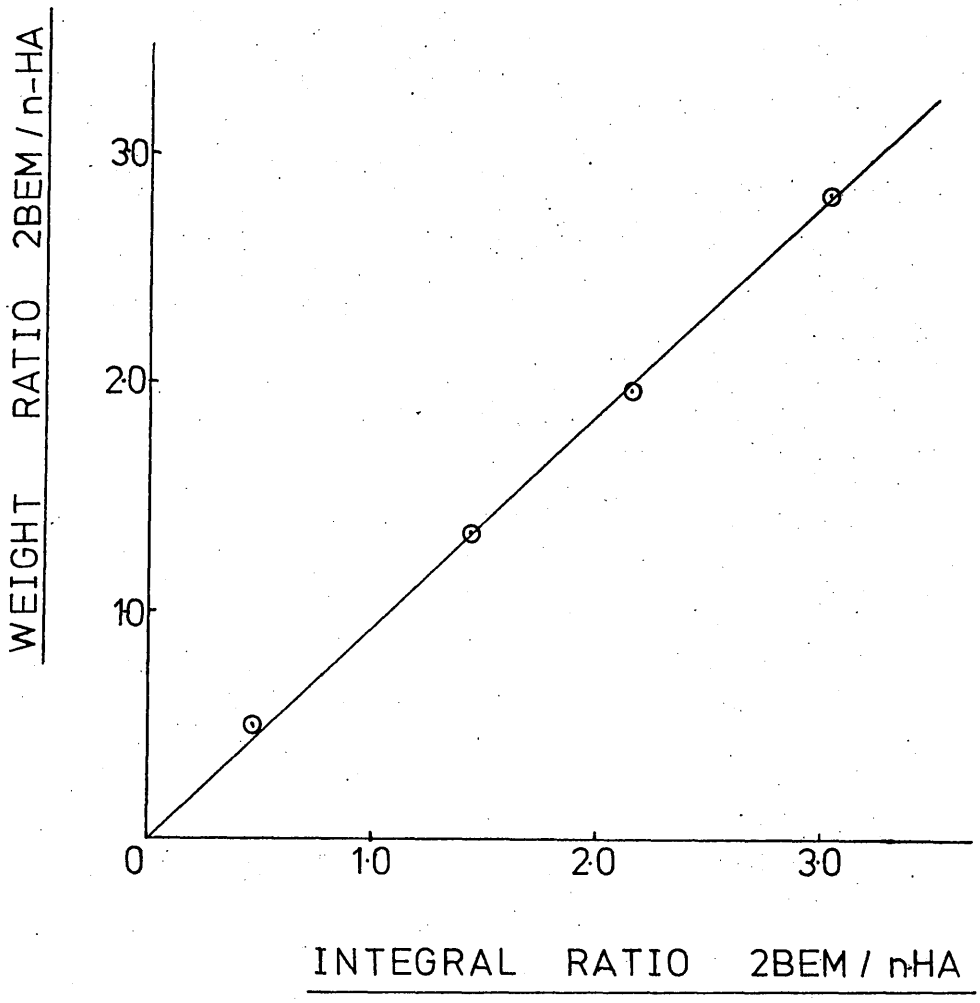


FIGURE 2.8 GLC CALIBRATION PLOT OF 2-BROMOETHYL METHACRYLATE USING n-HEXYL METHACRYLATE AS REFERENCE

by Perkin Elmer. After injection of the sample the columns were heated from room temperature to 150°C at a rate of 10°/min and held at that temperature until all the compounds passed through the detector. The carrier gas used was Helium at a flow rate of 40ml/min.

The production of acetaldehyde from P2BEA was measured quantitatively using the Microtek 2000R GC. The sensitivity factor K for this product using n-butanol as reference was found to be 2.27 by the method already outlined.

The columns used for this measurement were 9', × ½"o.d 1% carbowax on Silanised Embacell, and were heated isothermally at 50°C. The carrier gas was nitrogen.

Nuclear Magnetic Resonance Spectroscopy

Spectra were run in solution using $CDCl_3$ or CCl_4 as solvent, employing either the Varian T60 60MHz or the Varian HA 100 MHz spectrometer. For copolymer composition information, the average of six integrals was taken using the 100 MHz spectrometer.

2.6 Molecular Weight Measurement

Number average molecular weights were determined osmotically using a Mechrolab Model 501 High Speed Membrane Osmometer fitted with a Sylvania 300 grade cellophane membrane and using toluene as solvent. Osmotic pressures were made at a number of concentrations and the equation

$$\frac{\pi}{c} = \frac{RT}{Mn} + bc$$

applied. A plot of π/c vs c was drawn. Extrapolation of the graph to infinite dilution allows the number average

molecular weight Mn to be determined using the relationship

$$\frac{\pi}{c \to 0} = \frac{RT}{Mn}$$

This technique has a lower limit of ~25,000.

2.7 Microanalysis

Bromine contents were estimated using a Titration Method introduced by Cheng.

CHAPTER 3

DETERMINATION OF REACTIVITY RATIOS BY NUCLEAR MAGNETIC RESONANCE IN THE COPOLYMERISATION OF 2BEM AND MA

Reactivity ratios for the copolymer system 2BEM-MA have not been previously reported. Two methods of analysis could provide information on the relative molar concentration of each monomer in the copolymer, namely, Microanalysis and Nuclear Magnetic Resonance Spectroscopy.

3.1 Microanalysis

This technique gives information on the bromine content of the copolymer by the method outlined in Chapter 2. Theoretical monomer compositions of the copolymer were calculated and plotted against the corresponding percentage bromine values as in Figure 3.1. Percentage bromine data from microanalysis can then be inserted on to the curve and the corresponding molar ratio read off from the abscissa.

Table 3.1 shows the monomer ratios obtained by this method, where M_1 refers to 2-bromoethyl methacrylate monomer and M_2

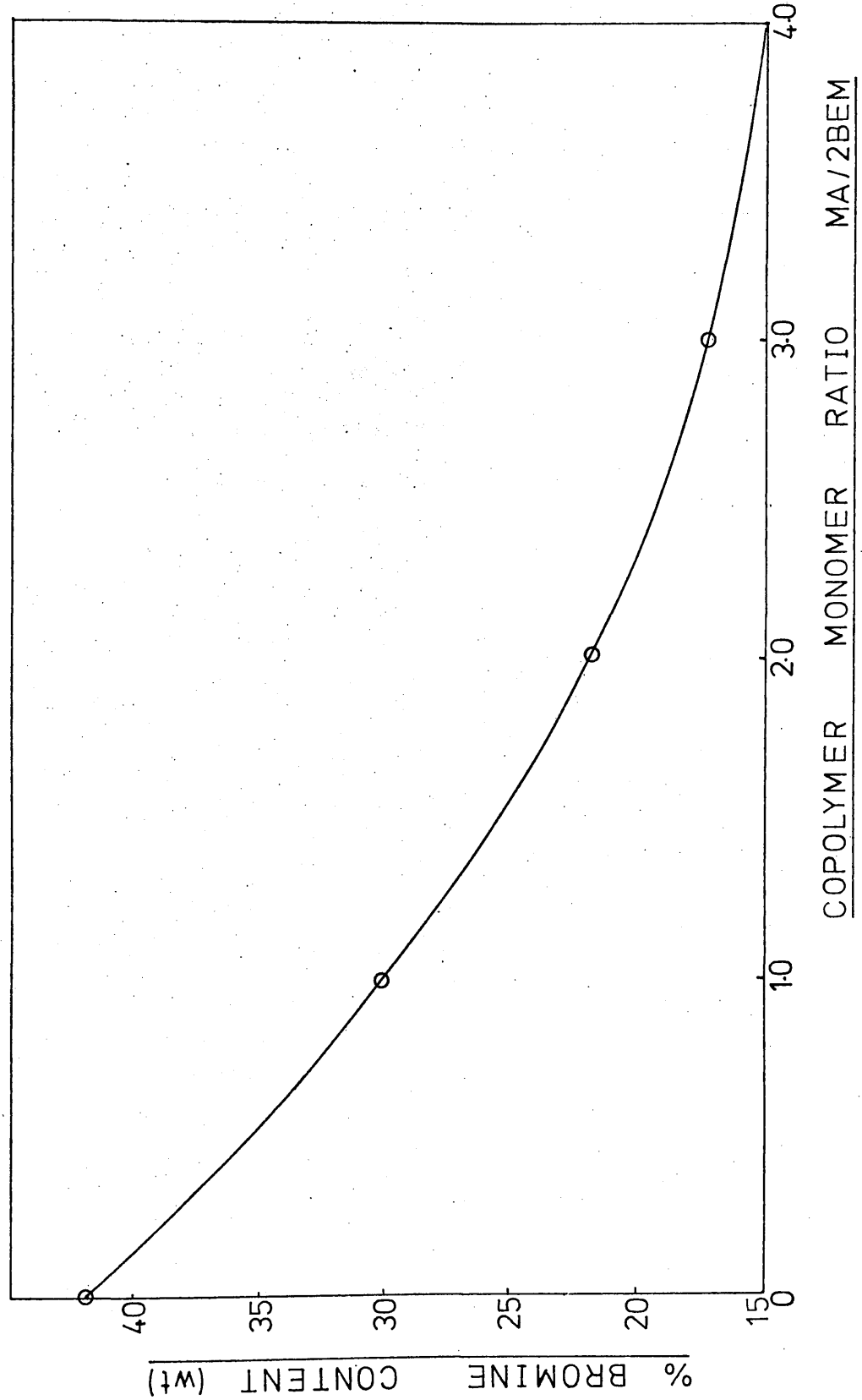


FIGURE 3.1 THEORETICAL CURVE OF BROMINE CONTENT vs COPOLYMER MONOMER RATIO FOR MA-2BEM COPOLYMERS.

refers to methyl acrylate.

Table 3.1 Copolymer Monomer Ratios by Microanalysis

Copolymer A	Monomer Molar Feed Ratio M_1/M_2	% Bromine Content	Molar Ratio In Copolymer M_1/M_2
1	1.463	36.1	2.78
2	0.588	33.4	1.74
3	0.268	26.5	0.80
4	0.022	6.6	0.08

This analytical technique gives bromine contents accurate to $\pm$ 0.5%. Therefore, the least accurate results were obtained for copolymers of low 2BEM composition. This inherent experimental error leads to less accurate copolymer compositions and ultimately inaccurate reactivity ratios. However, this technique could be used to check information obtained by the NMR method or where the spectroscopic method was not applicable.

3.2 Nuclear Magnetic Resonance Spectroscopy

Calculations of copolymer composition by nuclear magnetic resonance spectroscopy relies on the fact that absorptions of certain protons belonging to the respective monomers are sufficiently resolved to facilitate integral measurements. The monomer compositions of the copolymer may be calculated from the ratios of these integrals which are proportional to the number of protons contributing to the peaks. This method has been applied previously to elucidate reactivity ratios for the styrene - MMA system[43] and for methacrylate - acrylate copolymers.[44] Spectra were run as described in Chapter 2 using the average of six integrals from the 100 MHz spectrometer. Figure 3.2 shows

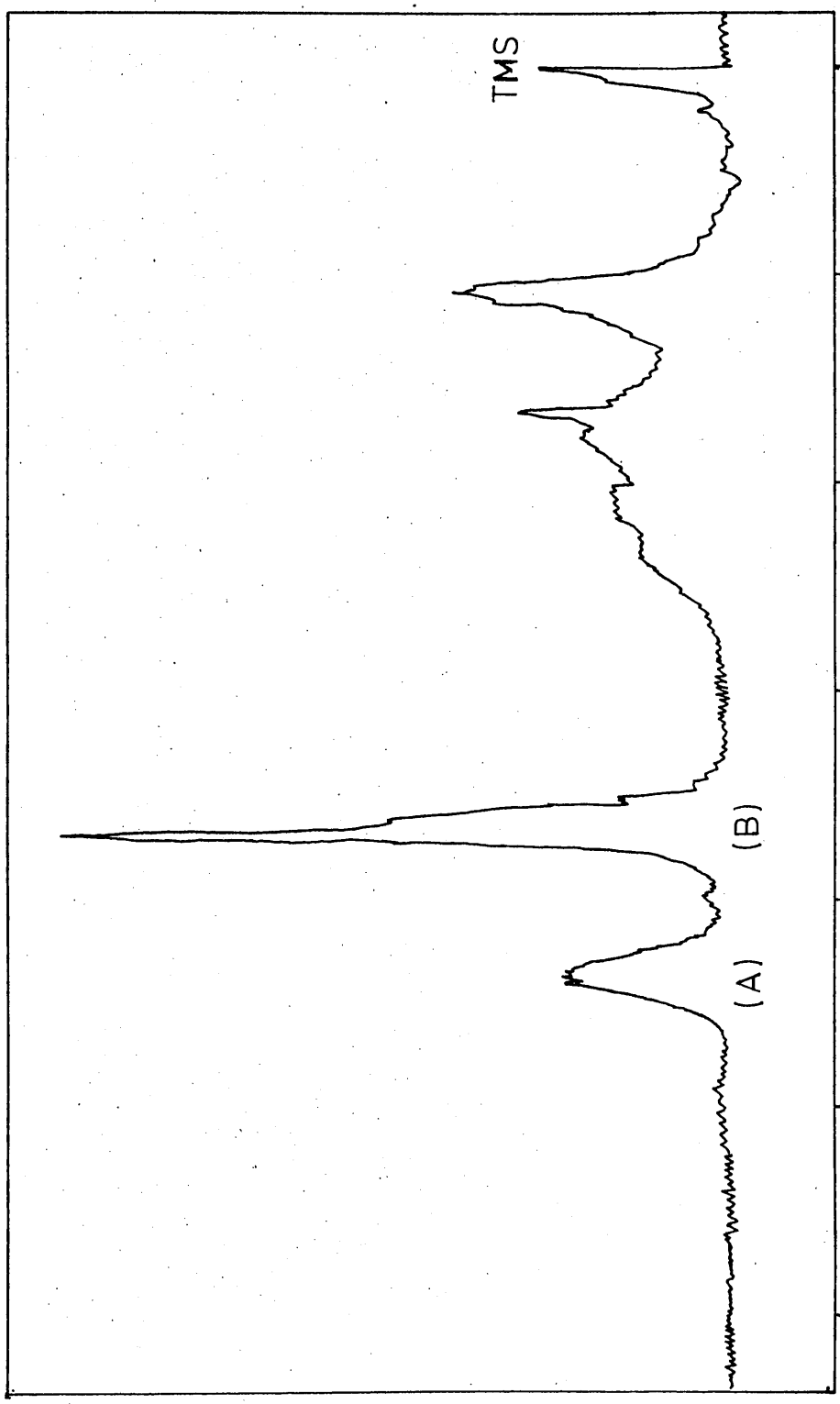


FIGURE 3.2 60MH$_2$ SPECTRUM OF COPOLYMER 2BEM-MA (A3)

the NMR spectrum of copolymer 3 of the 2BEM-MA system. Peak A at 4.35 is due to the O-$C\underline{H}_2$-protons of the methacrylate group. Peak B at 3.65 is a composite peak, due to the O-$C\underline{H}_3$ protons of the MA unit and the -$C\underline{H}_2$Br protons of the 2BEM group. Peaks A and B are sufficiently resolved for separate integral measurement. The integral due to the -$OC\underline{H}_3$protons may be calculated by subtracting the integral value of Peak A from the total integral due to peak B as the number of O-$C\underline{H}_2$- and -$C\underline{H}_2$-Br protons must be equivalent.

Hence, I-OCH_2 $\propto$ 2 (number of 2BEM units in the chain)

I-OCH_3 $\propto$ 3 (number of MA units in the chain)

where I-OCH_2- and I-OCH_3 are the integrals of the -OCH_2- and -OCH_3 peaks respectively.

If f is the molar ratio 2BEM/MA in the copolymer then

$$f = \frac{3\ (\text{I-OCH}_2\text{-})}{2\ (\text{I-OCH}_3)} = \frac{m_1}{m_2}$$

The ratios obtained by the above method gave the values for copolymer compositions shown in Table 3.2.

Table 3.2 Nuclear Magnetic Spectral Analyses

Copolymer	Monomer Feed Ratio M_1/M_2	$\frac{(\text{I-OCH}_2\text{-})}{(\text{I-OCH}_3)}$	Molar Ratio (f) in Copolymer
1	1.463	2.96	4.446
2	0.588	1.51	2.265
3	0.268	0.62	1.001
4	0.022	0.18	0.109

From the Values of M_1/M_2 and f (m_1/m_2) shown in Table 3.2 reactivity ratios were calculated by the method of Fineman and Ross,[45]

using the equations:-

$$\frac{F}{f}(f-1) = r_1 \frac{F^2}{f} - r_2$$

and $$\frac{(f-1)}{F} = -r_2 \frac{f}{F^2} + r_1$$

where $F = \frac{M_1}{M_2}$ (Monomer molar feed ratio)

$f = \frac{m_1}{m_2}$ (Copolymer monomer ratio)

r_1 and r_2 are the reactivity ratios of 2BEM and MA monomers respectively.

Plots of $\frac{F}{f}(f-1)$ versus $\frac{F^2}{f}$ (Figure 3.3) and $\frac{(f-1)}{F}$ versus $\frac{f}{F^2}$ (Figure 3.4) give reactivity ratio values of:-

$$r_1 = 2.77 \pm 0.03$$

$$r_2 = 0.19 \pm 0.02$$

The measurement of integrals becomes more difficult at the extremes of copolymer composition.

However, with the advent of higher resolution spectrometers, the composition of copolymer systems may be determined quickly, simply and accurately using the method outlined above, provided that proton signals from the respective monomers are sufficiently resolved.

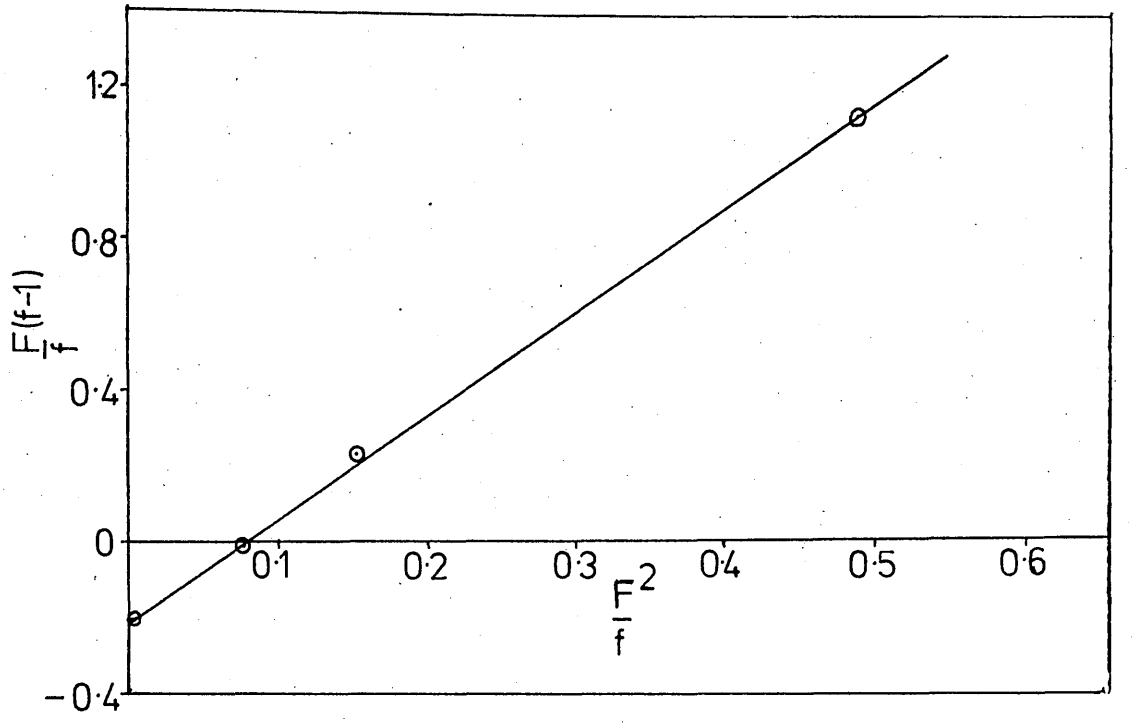


FIGURE 3.3 GRAPH OF $\frac{F}{f}(f-1)$ VERSUS $\frac{F^2}{f}$ FOR COPOLYMERS 2BEM-MA

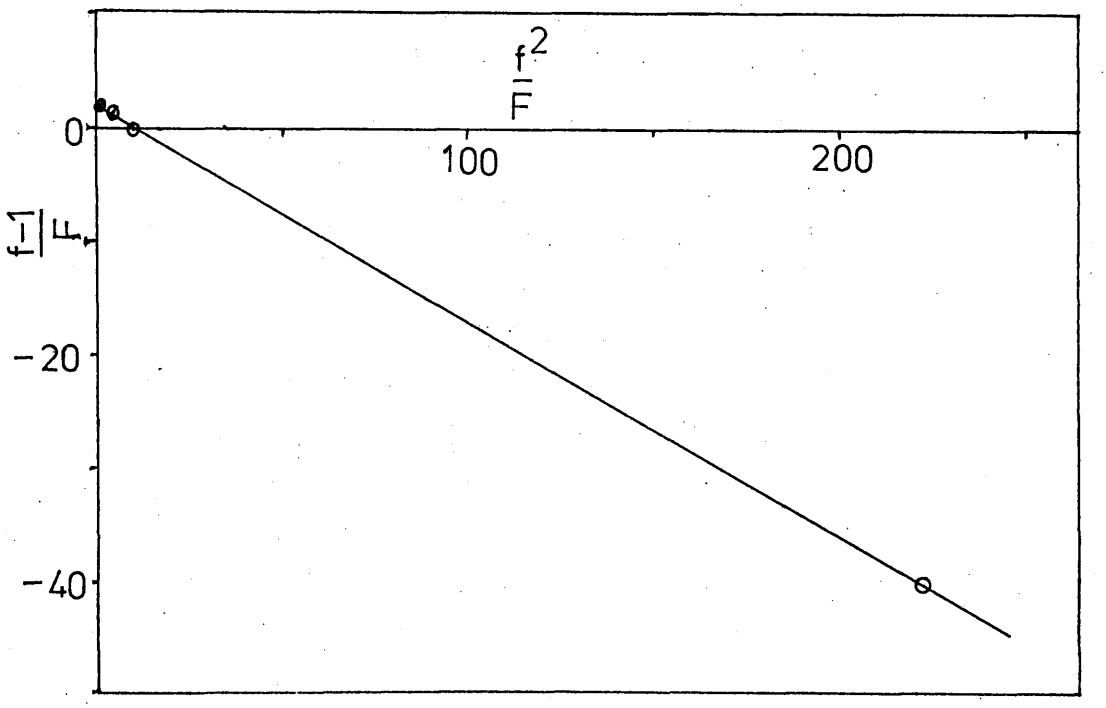


FIGURE 3.4 GRAPH OF $\frac{(f-1)}{F}$ VERSUS $\frac{f_2}{F^2}$ FOR COPOLYMERS 2BEM-MA

CHAPTER 4

THERMAL DEGRADATION OF POLY (2-BROMOETHYL METHACRYLATE) AND POLY (METHYLACRYLATE) HOMOPOLYMERS

4.1 INTRODUCTION

As discussed in Chapter 1 this present work has dealt exclusively with the brominated monomer 2BEM. Although no reports of previous investigations on the thermal stability of the homopolymer P2BEM could be found in the literature, there are a few patents[46,47] describing various recipes for commercial polymerisation mixtures which include 2BEM monomer, and the respective relative thermal stability and flammability properties of these polymers. Krause et al[48] synthesized the homopolymer P2BEM during their studies on the effect of the size of the side ester group on the glass transition temperature of a series of methacrylate hompolymers.

In this present work therefore, it is of primary importance to characterise completely each aspect of the thermal

behaviour of P2BEM. Once the mechanism of degradation of this system is fully understood then the effects of copolymerisation of different amounts of comonomer can be evaluated in terms of the respective homopolymer behaviour. A detailed account of the thermal degradation characteristics of PMA is also included in this chapter.

4.2 THERMAL ANALYSIS OF POLY(2-BROMOETHYL METHACRYLATE)

(a) TVA and Thermogravimetry

The TVA trace for this homopolymer is combined with the weight loss curve from thermogravimetry in Figure 4.1. This superposition of data clearly shows weight loss is concurrent with the production of material volatile at ambient temperature.

The TG curve obtained under nitrogen has three distinct stages, weight loss being complete by 390°C. The first stage occurs at $\sim$ 220°C, accounting for 4% of the total weight. The second begins $\sim$ 280°C with a further 6% weight loss. The remaining weight is lost in a single stage, reaching a maximum rate at 329°C.

The TVA thermogram shows two distinct peaks:- a small peak at 220°C and a much larger peak beginning at $\sim$ 250°C and reaching a maximum rate of volatilisation (T_{max}) at 330°C. A sholder at $\sim$ 280°C is observed on the main peak.

Up to 300°C only the TVA trace at 0°C moves above the baseline. This large separation of trap traces indicates virtual exclusive production of a single high boiling product condensed by the -45°C trap.

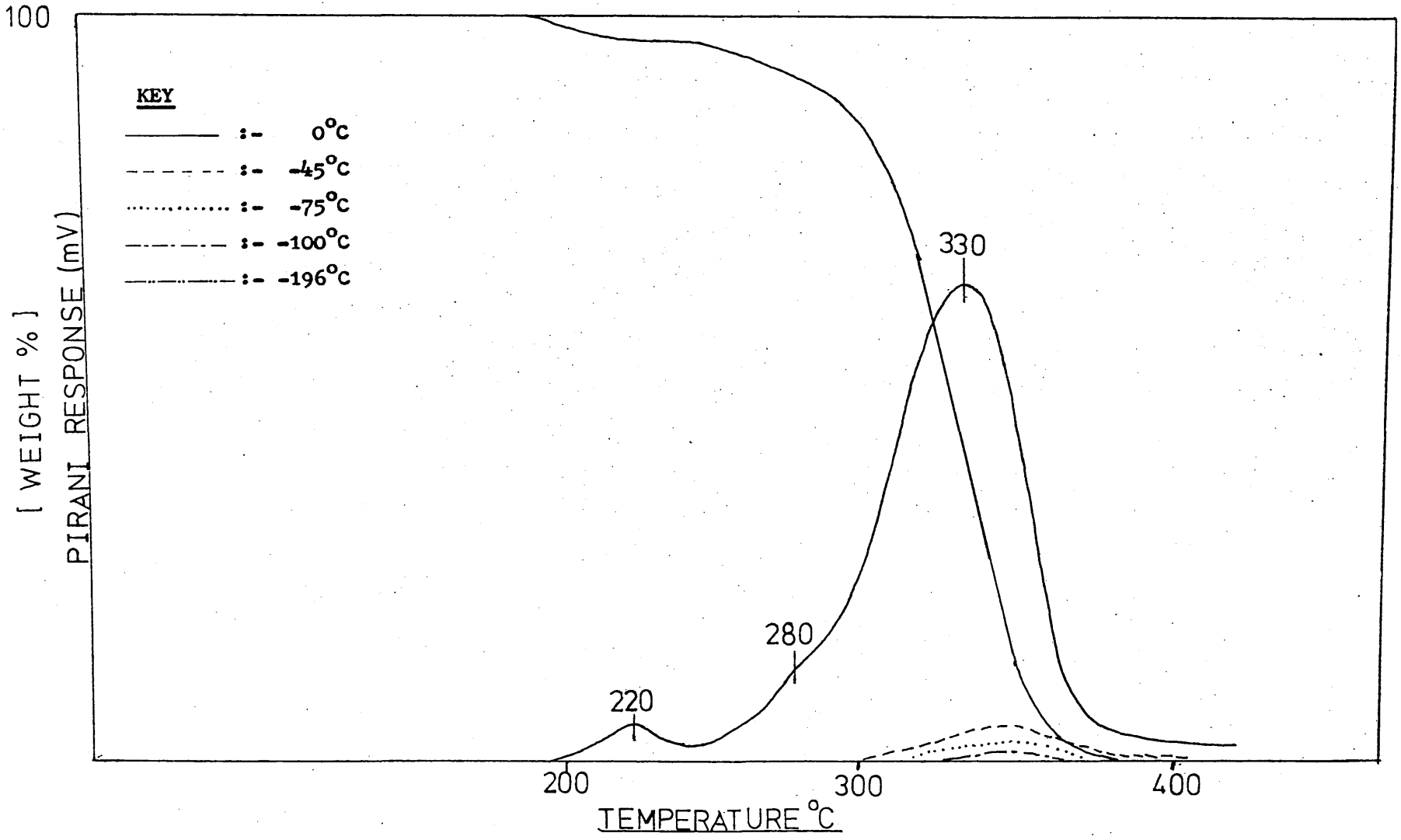


FIGURE 4.1 COMBINED TG & TVA CURVES FOR P2BEM (60 mg POWDERED SAMPLE).

The traces due to the -45°C, -75°C and -100°C traps do leave the baseline, however, just over 300°C reaching a maximum at 350°C. The fact that this temperature is not the same as T_{max} suggests that the reaction which gives rise to these volatiles is independent of the main volatilisation reaction. The thermogram indicates no porduction of non-condensable products during programmed degradations. Other features of the degradation include no formation of any 'cold ring' fraction and only trace amounts of residue remaining at 500°C.

(b) Differential Thermal Analysis and Differential Scanning Calorimetry

Both of these techniques afforded similar information; the DSC curve is illustrated in Figure 4.2. The small endotherm at 77°C is due to the glass transition. This value differs from the value of 52°C obtained by Krause et al.[48], who used a dilatometric method to evaluate Tg, involving measurements at equilibrium at various temperatures. As the time scale of measurements varies drastically from that employed in thermal analysis the results of the two methods are not strictly comparable.

The major endotherm, which begins at approximately 250°C, has a small shoulder at 280°C, peaks at 329°C and is completed by 400°C. This endotherm corresponds to the volatilisation reaction.

(c) Product Analysis

As suggested by TVA, the major product of degradation is found to be monomer. This was confirmed by infra-red analysis, both in the gas and liquid phase of volatile products. Traces

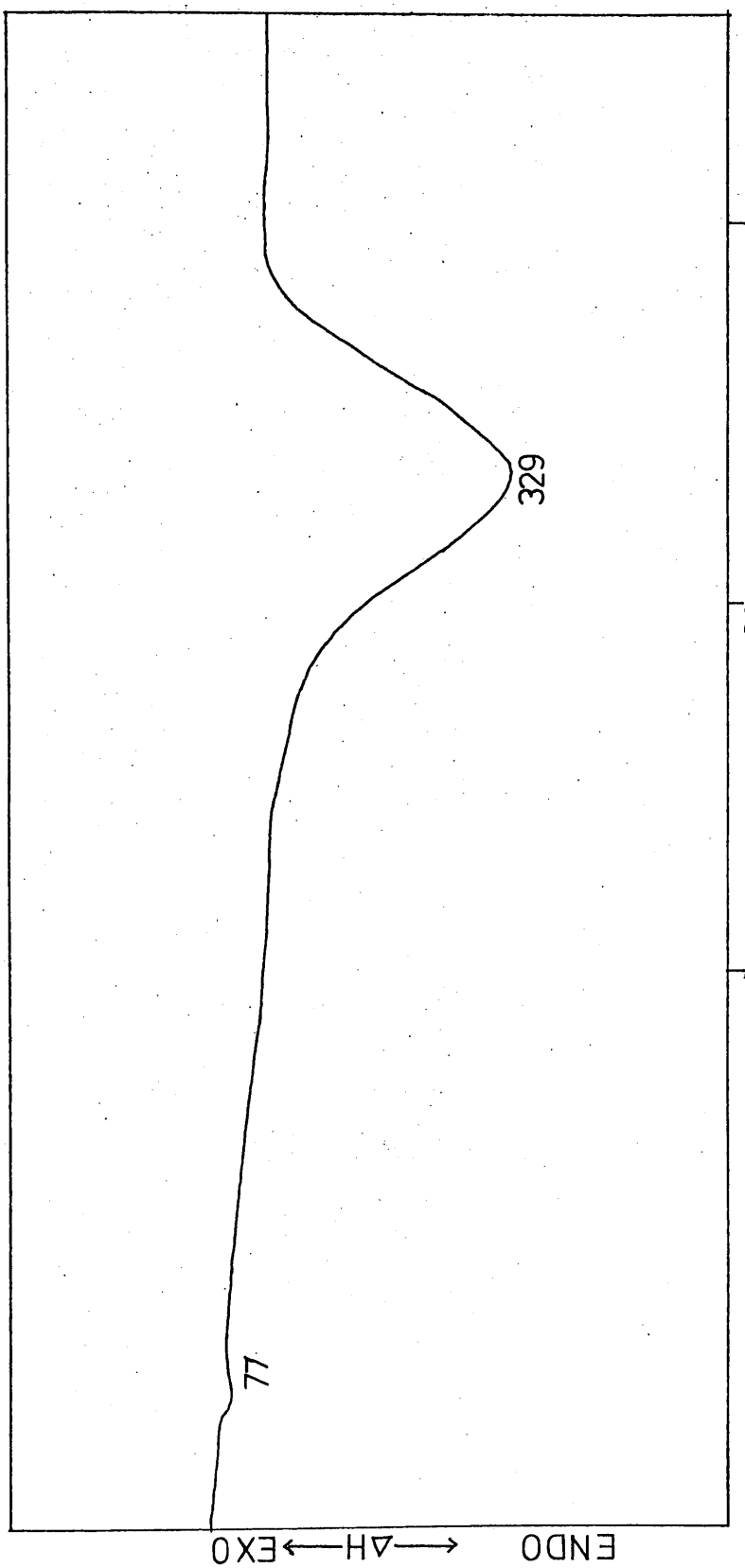


FIGURE 4.2 DSC OF POLY(2-BROMOETHYL METHACRYLATE).

of carbon dioxide and vinyl bromide were detected by the sub-ambient distillation of degradation products from a 60mg sample of homopolymer. The distillation trace is shown in Figure 4.3: the quantities, which are barely detectable by infra-red spectroscopy, are certainly less than 1% of the original polymer sample weight. Monomer accounted for over 93% of the original weight.

(d) Discussion

In order to explain the occurrence of the small peak at $\sim$ 220°C in TVA, dynamic degradations were carried out to 225°C and the products distilled under sub-ambient conditions. Subsequent analysis showed that monomer was the only product formed, and it was concluded that this was occluded monomer from the polymerisation process. It does not volatilise until this temperature because of its high boiling point. Further evidence for this explanation lies in the fact that both DTA and DSC fail to respond to this volatilisation reaction. This behaviour suggests that the monomer produced at that low temperature is not part of the polymer chain system.

As monomer is virtually the exclusive degradation product, the mechanism of degradation must be similar to that of PMMA discussed earlier. However the degradation of P2BEM does differ from that of PMMA in two ways:-

(i) The T_{max} of P2BEM occurs some 40°C lower than that of PMMA. This relative instability may be due to the steric effect of the bulkier brominated side group. This larger

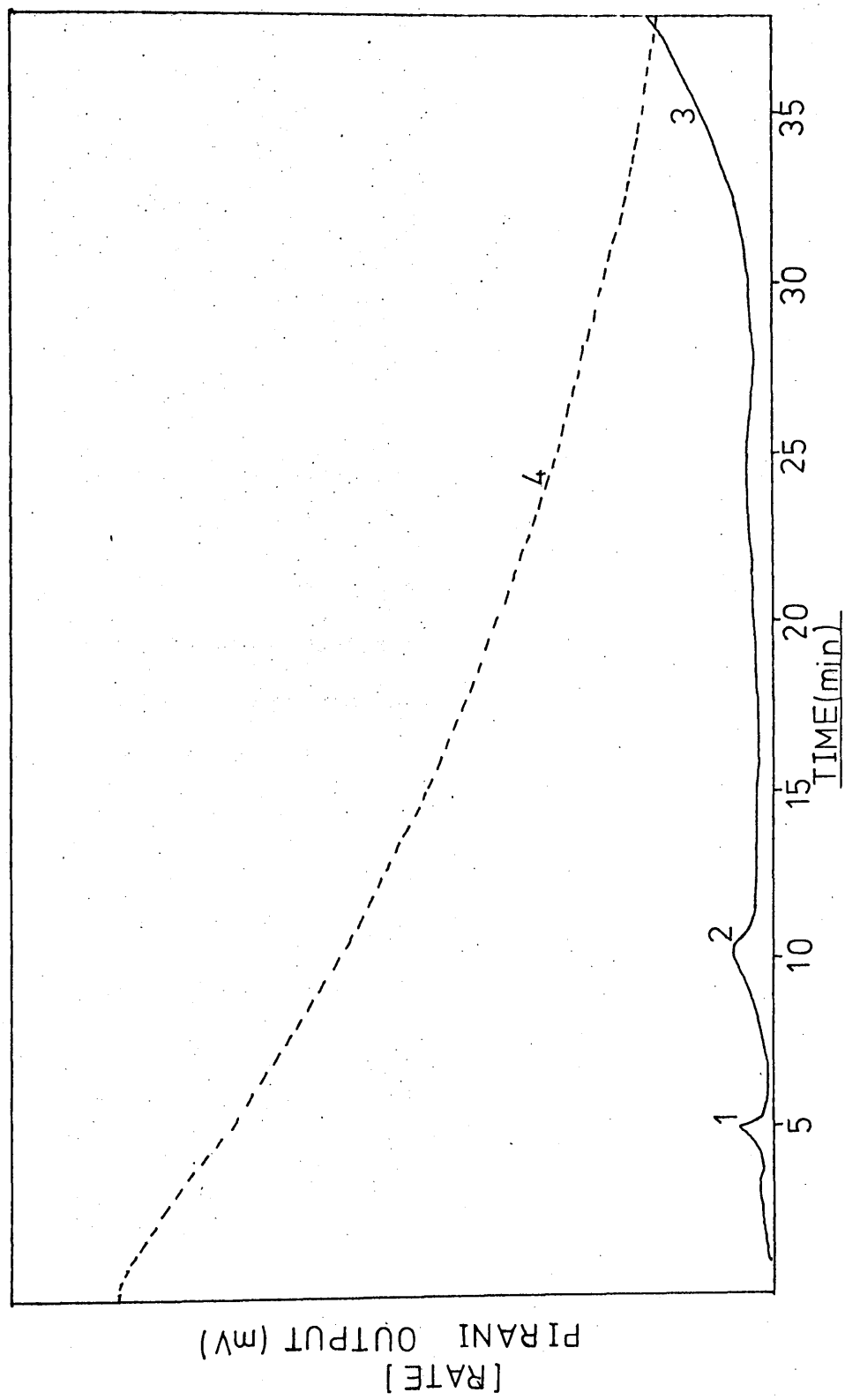


FIGURE 4.3 SUB-AMBIENT DISTILLATION CURVE FOR 61.4 mg P2BEM DEGRADATION PRODUCTS

1: CO_2 2: $CH_2{=}CHBr$ 3: MONOMER 2BEM 4: SUB AMBIENT THERMOCOUPLE OUTPUT (-MV)

side group not only increases the flexibility of the chain, manifested in the lowering of Tg, but increases the steric crowding of neighbouring groups. Depolymerisation, therefore, occurs at this lower temperature to release this added steric strain energy factor.

This result substantiates earlier work by Crawford[49] who showed that the rate of depolymerisation at 250°C of a number of n-alkyl methacrylates increases with increasing size of the side group.

(ii) The formation of carbon dioxide and vinyl bromide in trace quantities suggests that ester decomposition occurs to a small extent. As discussed earlier in Chapter 1, the relative importance of this reaction depends on the number of β -hydrogen atoms on the side chain available for formation of 6-membered transition states.[50,51] The 2-bromoethyl ester has two such protons available for reaction, and so in accordance with previous findings,[50] side-chain cracking occurs to a small degree.

Nevertheless, this reaction may become competitive with depolymerisation if isolated 2BEM units are exposed to temperatures greater than those at which depolymerisation normally occurs.

An interesting aspect of this homopolymer system is the fact that the carbon-bromine bond on the side chain does not undergo scission at any stage of the degradation. On the basis of bond dissociation energies, it would seem that this bond is the most likely to be broken. However, carbon-

carbon bond scission occurs preferentially allowing depolymerisation to take place. This instability seems to be a function of the macromolecular chain structure, whereas the carbon-bromine bond appears on the side group and is not part of this polymeric structure, and may, therefore, retain its thermal stability right up to depolymerisation temperatures.

Thus, the homopolymer poly(2-bromoethyl methacrylate) would seem, from all the evidence, to undergo a free radical depolymerisation reaction, initiated at low temperatures by unsaturated chain-end structures and at higher temperatures by main chain scission, giving monomer almost quantitatively. At higher temperatures, trace amounts of carbon dioxide and vinyl bromide are produced from ester decomposition of the side chain. Volatilisation is complete by 400°C, leaving only trace amounts of residue.

4.3 THERMAL DEGRADATION OF POLYMETHYL ACRYLATE

The PMA sample used in this work was polymerised in solution by the general method outlined in Chapter 2 and had an average molecular weight of 617,000.

(a) Thermal Volatilisation Analysis

The TVA thermogram of PMA (Figure 4.4) shows a single main peak followed by a low plateau. The threshold temperature for volatilisation is 325°C with T_{max} occurring at 416°C. All the traces are separated to some extent, suggesting that products of varying volatility are being evolved during the degradation. There is significant separation, however, of

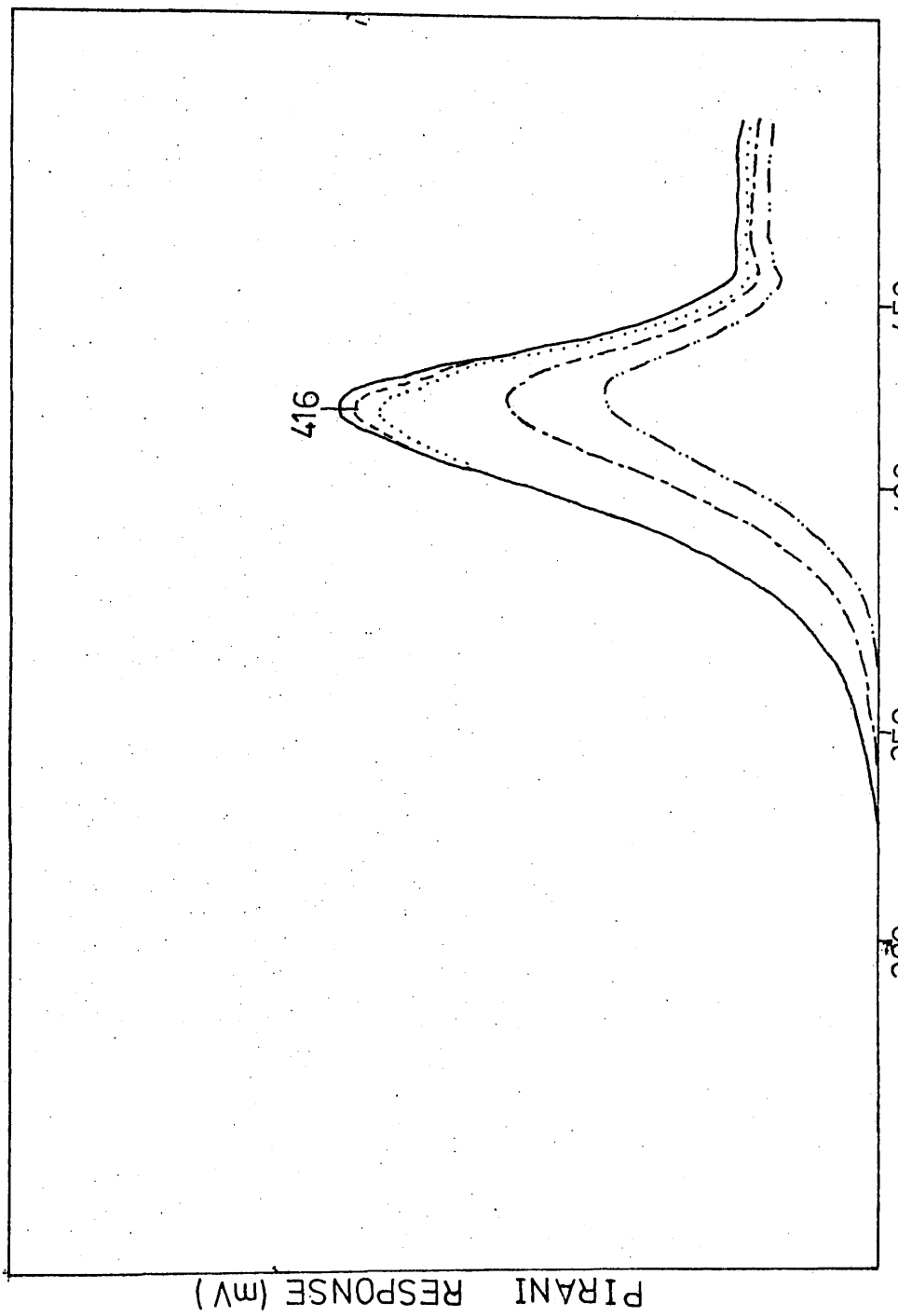


FIGURE 4.4 TVA TRACE OF 25 mg PMA (10^{o}/min).

the -75°C and -100°C traces, as well as the -100°C and -196°C traces. This evidence implies that small volatile molecules are being produced at this stage.

The -196°C trace indicates that non-condensable products are also being formed.

A substantial 'cold ring' fraction was coloured deep yellow and dissolved in carbon tetrachloride for infra-red spectroscopic analysis.

A very small amount of residue remained at 500°C accounting for only a few per cent of the original weight.

(b) Thermogravimetry and Differential Scanning Calorimetry

The TG curve for PMA is shown in Figure 4.5. The trace clearly indicates that weight loss occurs in a single stage leaving about 2% residue at 460°C. Weight loss begins at approximately 330°C reaching a maximum rate at 408°C. This information confirms that the weight loss reaction corresponds to volatilisation as shown in TVA. Figure 4.5 also illustrates the DSC curve of PMA, showing one endotherm corresponding to the weight loss reaction. The endotherm reaches a maximum value at 407°C, comparing favourably with the temperature of maximum rate of weight loss (408°C) from TGA.

(c) Product Analysis

Qualitative analysis of the component peaks from the sub-ambient TVA curve (Figure 4.6) was carried out using infra-red spectroscopy. These peaks were identified as (1) carbon dioxide, (2) methanol and some monomer and (3) short chain fragments of polymer.

Although no quantitative estimation of products was carried

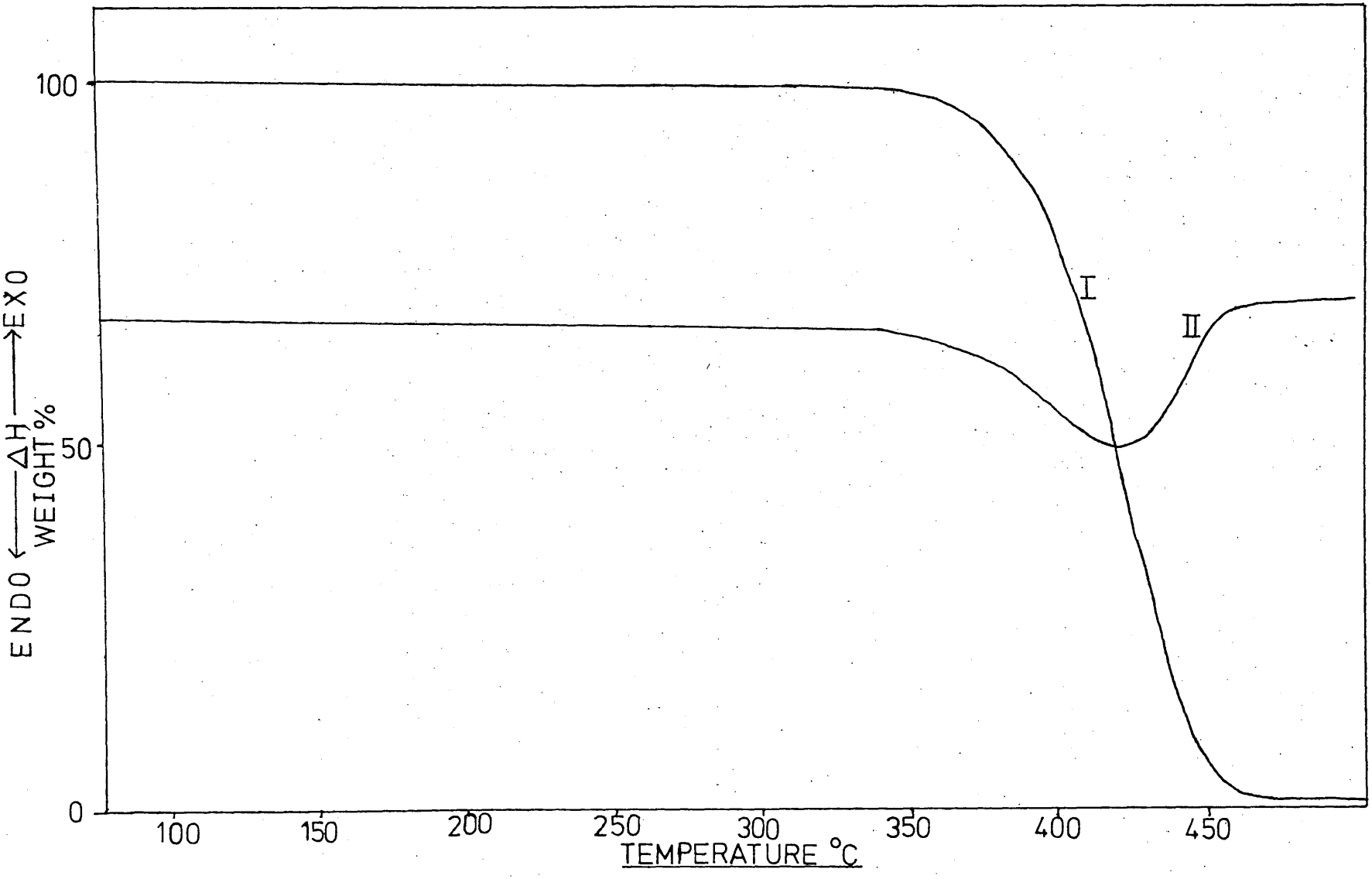


FIGURE 4.5 COMBINED TG(I) AND DSC(II) CURVES FOR PMA 10°/min IN N_2 (80ml/min).

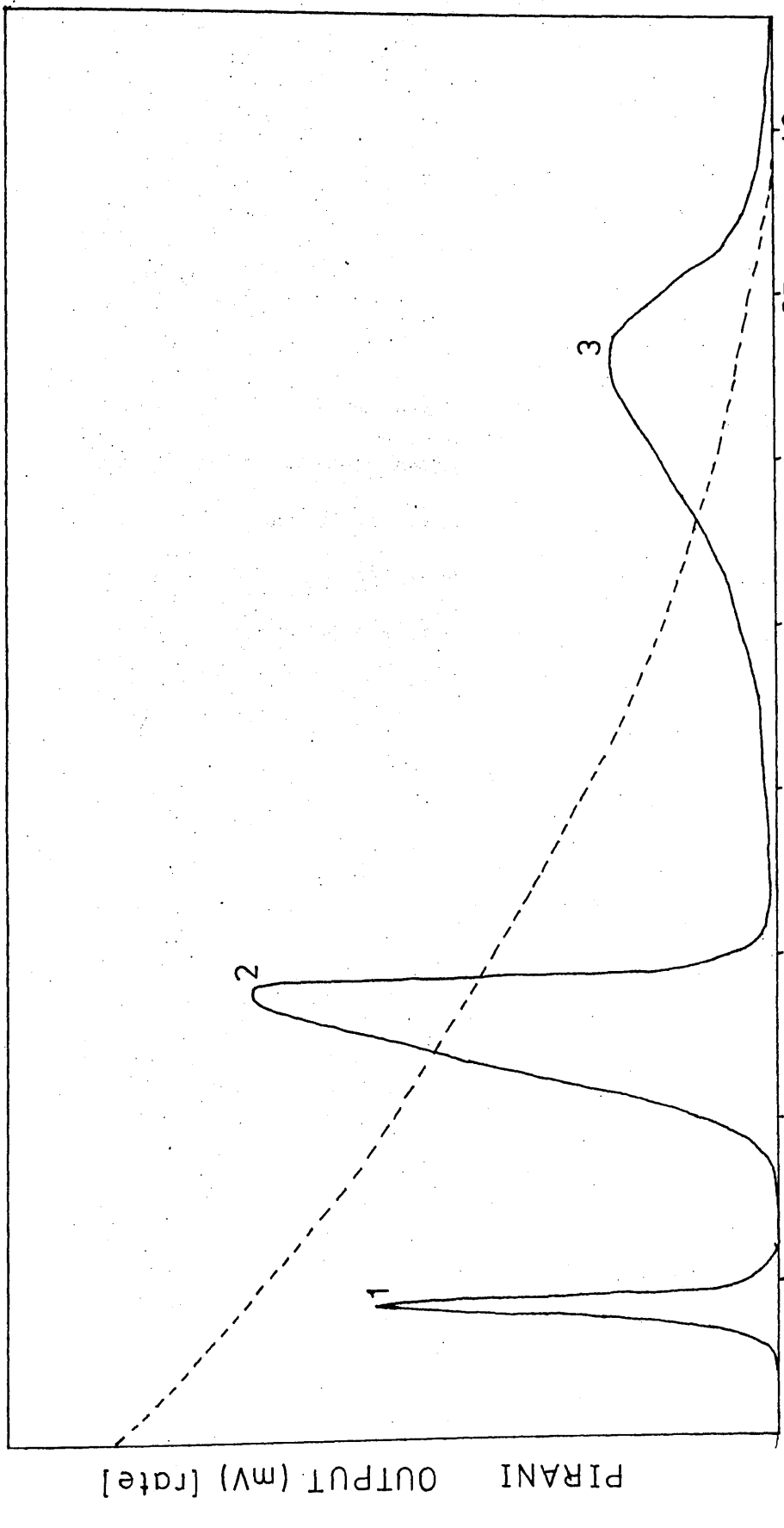


FIGURE 4.6 SUB-AMBIENT TVA TRACE FOR DEGRADATION PRODUCTS OF PMA (20 mg) DEGRADED TO 500°C at 10°/min

1: CO_2 2: METHANOL AND SOME MONOMER 3: SHORT CHAIN FRAGMENTS.

out the production of methanol was in excess of that of carbon dioxide, as indicated in Figure 4.6.

The third peak in the sub-ambient distillation curve was identified as short chain fragments of the original polymer, possibly dimer or trimer. These fragments were sufficiently volatile to reach the cooling traps. The bulk of the degradation products, however, were found in the 'cold ring' fraction and identified as chain fragments resembling the original polymer in most ways, but with the following exceptions:-

(i) This fraction was coloured yellow; showing increased absorptions in the carbon-carbon double bond region of the infra-red spectrum and in the UV range of 250-400 nm.

(ii) A broadening of absorption in the carbonyl region of the infra-red spectrum was observed, shoulders appearing at both higher and lower frequencies than those of the original polymer carbonyl.

(iii) Absorptions in both the carbonyl and carbon-oxygen stretching regions were reduced.

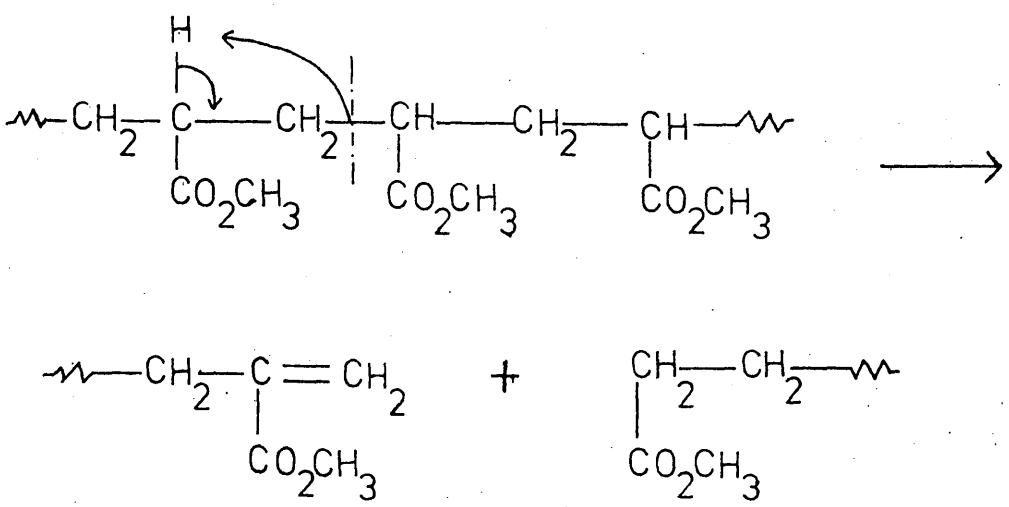
Another feature of the degradation of PMA was the partial formation of an insoluble gel after a small degree of volatilisation. The degree of insolubility increased with increasing amounts of volatilisation.

(d) Discussion

It is important at this point to review the general features and degradation products of the thermal decomposition of poly (methyl acrylate).

The thermal degradation of PMA was first studied by Straus

and Madorsky[52] who quantitatively examined various fractions from degradations carried out at temperatures between 250°C and 400°C. They found that the main product of degradation (73% by weight) was a low polymer fraction with an average molecular weight of 633. Other volatile products identified were methanol (15%), carbon dioxide (7.5%), methyl acrylate (0.7%), methyl methacrylate (0.1%) and C_4-C_6 oxygenated compounds (3.9%). Madorsky[53] concluded that because little monomer is formed the mechanisms of the thermal degradation reactions do not involve free radicals but may be explained by the following disproportionation reaction:-



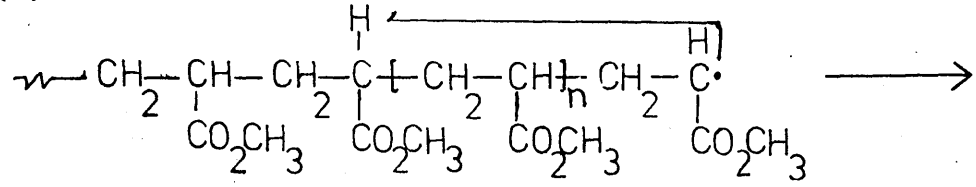
Further work by Madorsky[54] suggested that chain scission in the temperature range 285-300°C was a random process with an activation energy of 37 Kcal/mole.

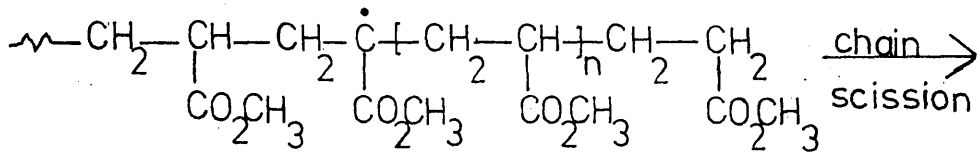
Cameron and Kane[55] measured the molecular weight of the residue at various stages of the reaction and concluded that the results supported Madorsky's view of a random chain scission process, but did not exclude the possibility of'weak links'. Also, the formation of an insoluble gel, indicative of cross-linking, was found to increase with increasing extent of

volatilisation.

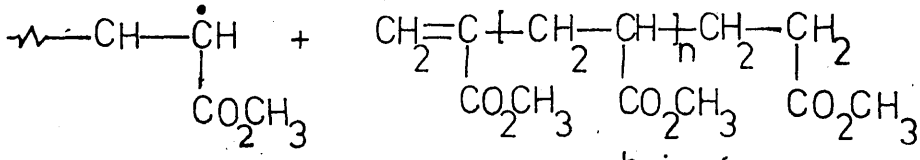
The same authors studied the effect of the radical inhibitor 1, 4, diaminoanthraquinone on the chain scission and volatilisation reactions.[56] On the basis of their results they proposed that low polymer formation may be explained by random homolytic backbone bond scission followed by a chain of free radical transfer reactions, both inter-and intramolecular, as indicated below:-

(i) Intramolecular Reaction

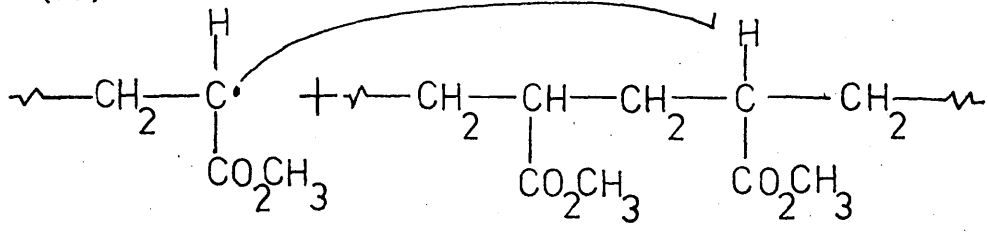


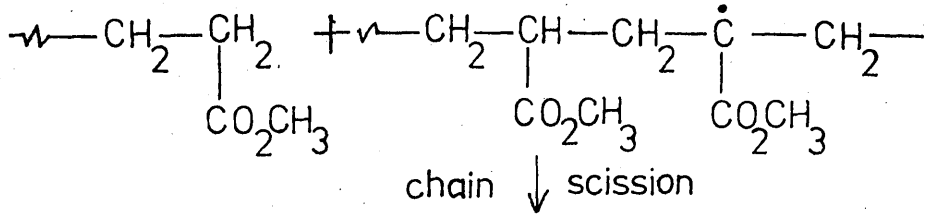


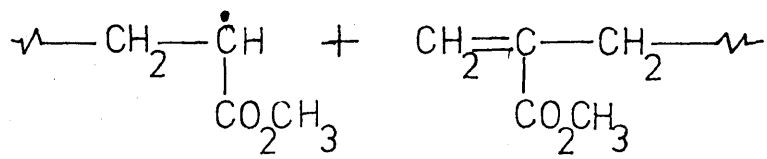
(A)



(ii) Intermolecular Reaction

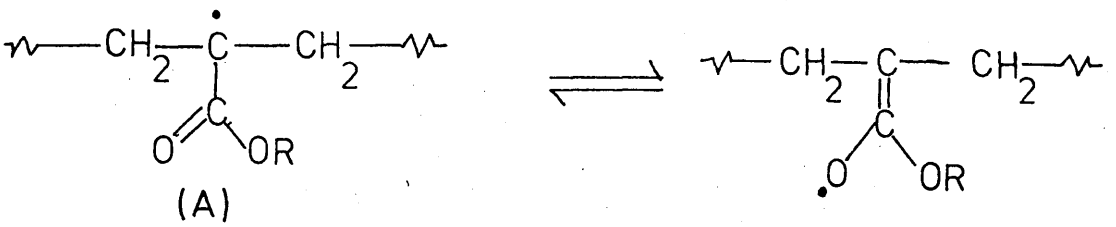






The intramolecular process was described as 'unbuttoning", in which a radical moves along the polymer chain eliminating chain fragments larger than monomer, in contrast to 'unzipping' in which monomer units are progressively eliminated, as in the degradation of PMMA. The relative importance of the two processes was difficult to estimate. However, as chain fragments are the main degradation products, the intramolecular process was thought to dominate. Nevertheless, the effect of the inhibitor on molecular weight changes did indicate that the intermolecular transfer step certainly does take place. Initiation was thought not to originate at chain-end structures as the rate of volatilisation does not change when the number of chain-ends per unit weight is increased. Random cleavage of the back-bone was believed to be the most probable initiation step.

Cameron and Kane[57] then considered possible mechanistic pathways to explain the formation of the volatile products from degradation as well as crosslinking and colouration. The most logical starting point was polymer radical (A), formed in both the transfer steps in the fragmentation process.

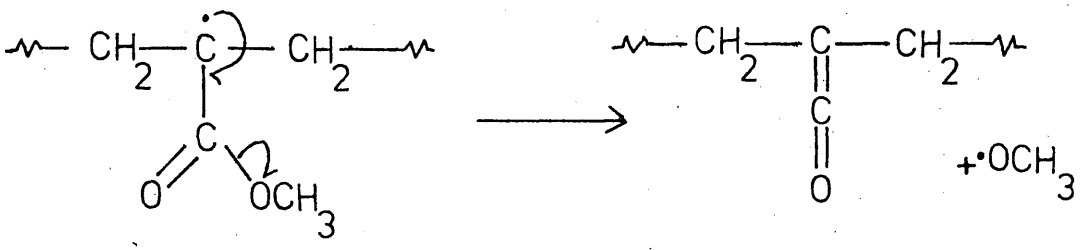


(A)

This radical can be stabilised by delocalisation with the adjacent carbonyl group as shown. It was suggested that this radical is the common free radical precursor for the formation

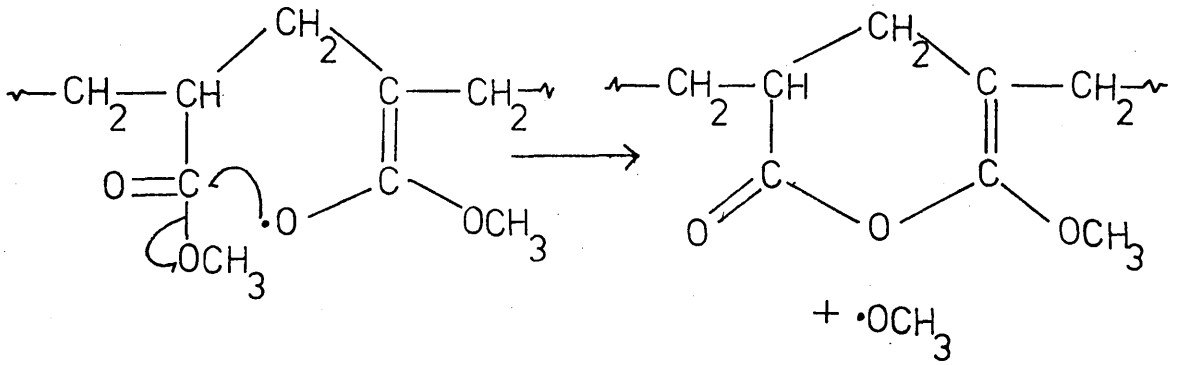
of carbon dioxide, methanol and low polymer, and that the formation of these products represents competing steps in the free radical chain reaction.

A number of reaction routes for the formation of methanol were considered involving radical (A). The first involves the formation of a ketene structure with elimination of a methoxy radical:-



This mechanism, however, could not be supported as no ketene absorptions could be detected at 2160cm^{-1} in the infra-red spectrum of the residue.

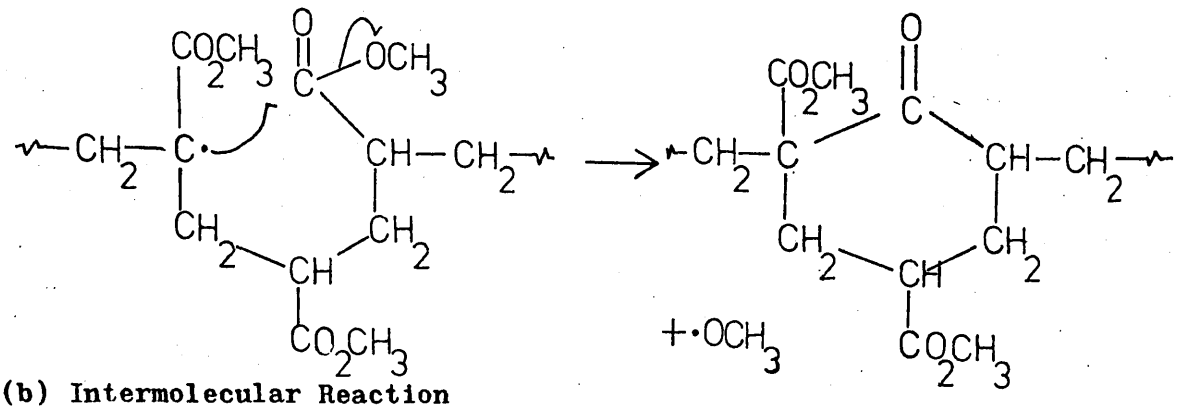
The second possible route is an intramolecular displacement reaction using the resonance form of radical (A) to form a γ, δ unsaturated δ - lactone ring system or an ester if the reaction occurs intermolecularly.



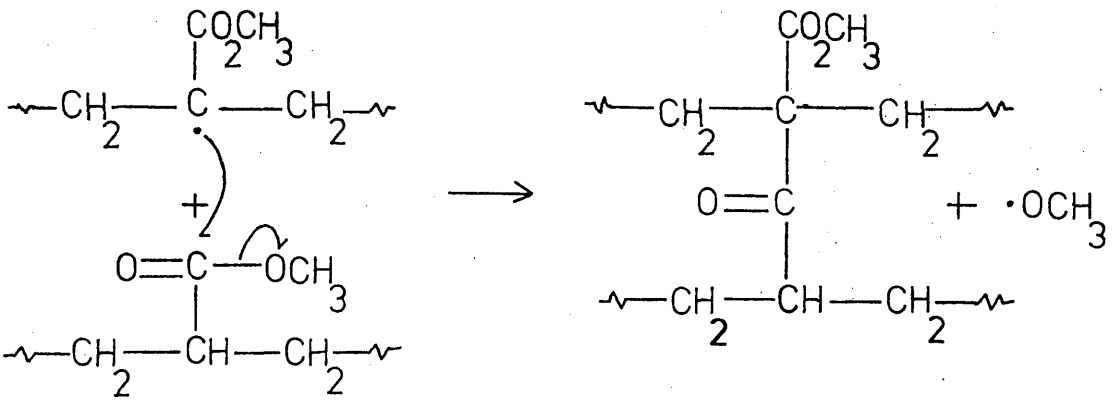
Support for this mechanism is found in the carbonyl region of the infra-red spectrum which shows a shoulder developing at 1760cm^{-1} suggesting the presence of an unsaturated lactone.

The third possibility involves the formation of a nonenolisable β-ketoester which may be in a six membered ring if the reaction occurs intramolecularly, or acyclic if it occurs intermolecularly.

(a) Intramolecular Reaction



(b) Intermolecular Reaction



The eliminated methoxy radical would then abstract a proton, possibly a tertiary hydrogen atom, to form methanol and regenerate the polymer radical (A).

The third mechanism also receives support from infra-red spectroscopy, a shifting of the main carbonyl peak to a lower frequency in accordance with the proposed structures.

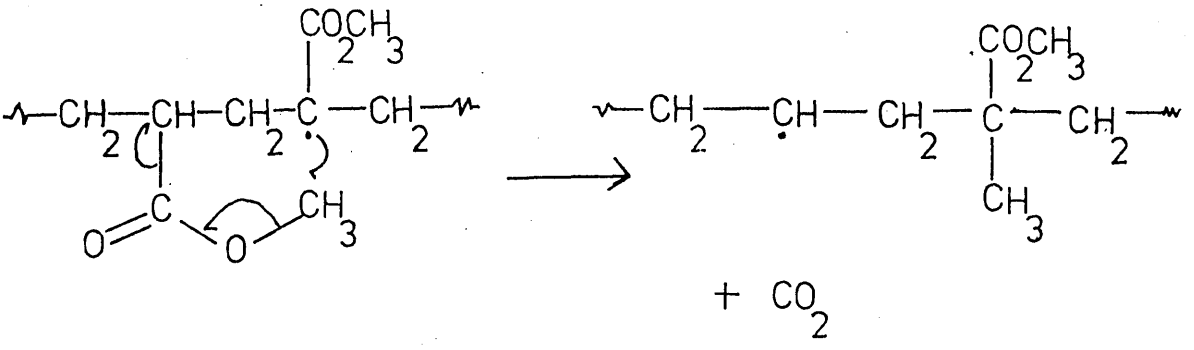
The intermolecular reaction would produce a crosslinked structure which would explain gel formation.

It is noted that mechanism 2 involves the interaction of

adjacent MA groups whereas mechanism 3 requires three consecutive MA units for a methoxy radical to be displaced. A study of the thermal decomposition properties of MMA-MA copolymers by Grassie and Torrance[58,59], demonstrated that at least three sequential MA units were required for methanol formation. This conclusion is in accordance with the thermal break-down of ethylene-methyl acrylate block copolymers[60] which produce methanol in the quantities expected from the methyl acrylate content while random copolymers of the same overall composition produce very much less. Strassburger et al[61] also investigated MMA-MA copolymers and found methanol present in the degradation products. However, these copolymers were polymerised to 100% conversion so that blocks of MA units will inevitably be present.

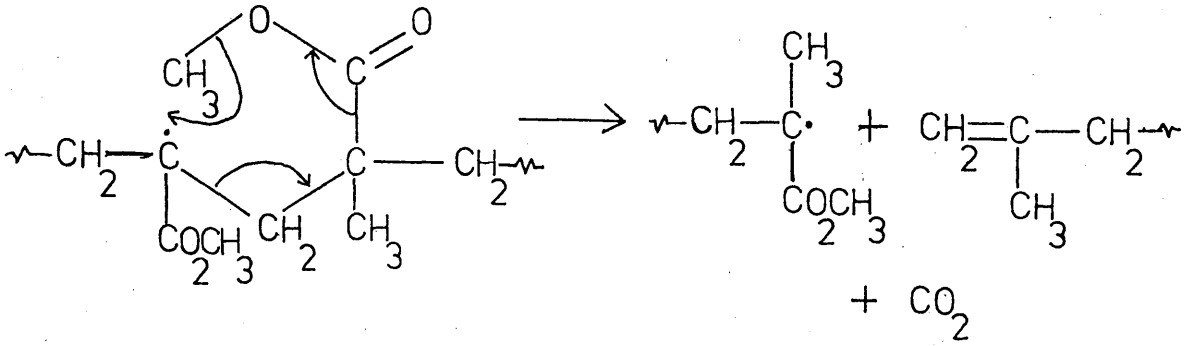
The bulk of evidence therefore, strongly supports the third mechanism although to what extent the intermolecular reaction contributes to the overall reaction is difficult to estimate. It will however, be manifested in the degree of gel formation as degradation proceeds.

A mechanism first suggested by Fox and his colleagues[62] is used by Cameron and Kane[57] and Grassie and Torrance[59] to explain the production of carbon dioxide in degradation systems involving methyl acrylate units.



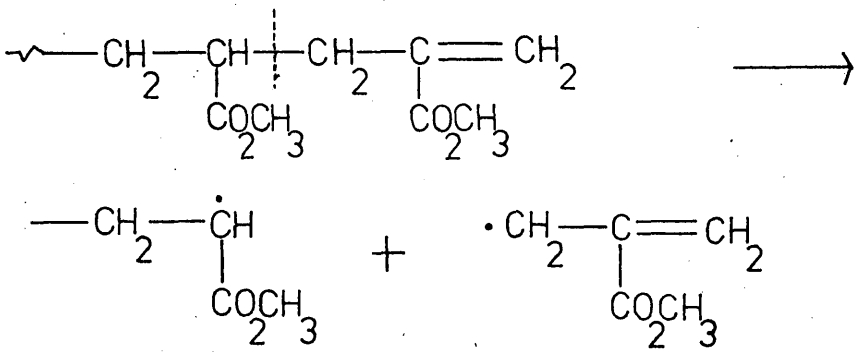
Previously, evidence for this reaction was provided by the existence of methyl methacrylate monomer among the degradation products. Grassie et al[18] however, found no trace of the corresponding α - substituted acrylate in the degradation products of a series of poly (alkyl acrylates).

Grassie and Torrance[59] took the carbon dioxide formation reaction a step further in their study, relating it to chain scission.



In their study it was suggested that carbon dioxide formation is a property of individual MA units, and may even involve the methylene protons on the back-bone.

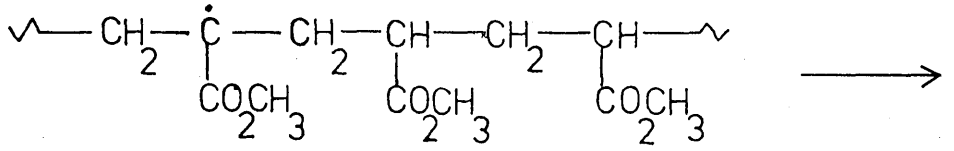
The existence of small amounts of the corresponding methacrylate monomer in the products may arise from the carbon dioxide reaction[57] but later work[18] suggests that the unsaturated chain-end structures may be the more likely formation site.

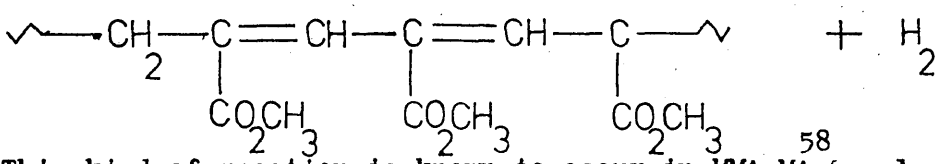


The bond β to the double bond being particularly vulnerable to attack. Formation of methyl acrylate monomer exceeds that

of methacrylate and probably arises by depropagation from an acrylate terminated polymer radical, although this is known to be only a very minor reaction in polyacrylates.[18]

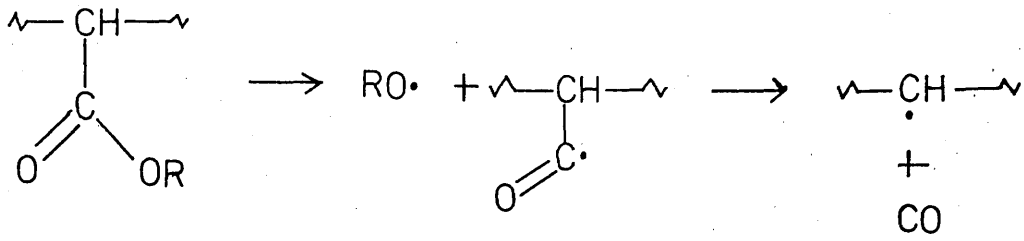
Cameron and Kane[57] explained the build up of colour during degradation by the formation of conjugated sequences of carbon-carbon double bonds in the back-bone. These may be formed by the elimination of hydrogen atoms by polymer radical A in a reaction analogous to the loss of hydrogen chloride from polyvinyl chloride.[63] Thus, hydrogen will be liberated from sequences of MA units resulting in conjugation.





This kind of reaction is known to occur in MMA-MA copolymers[58] as well as polyethylene[64] and polystyrene[65] under high energy and ultra-violet irradiation respectively, and it has been suggested that it may be a general reaction of ethylenic type addition polymers. Very little hydrogen was observed,[57] however, so that the reaction in PMA homopolymer is comparitively unimportant quantitatively. This mechanism has been used to explain the occurrence of hydrogen and methane in the decomposition products,[58] for MMA-MA copolymers. In related work on poly (benzyl acrylate) Cameron and Kane[66] showed that more extensive internal unsaturation develops, and hydrogen is detected among the gaseous reaction products. Carbon

monoxide is a minor product from PMA degradation[18] and may be simply explained by homolytic scission of the acyl-oxygen bond to form a carbonyl radical, which is very unstable[67] and will decompose immediately to give carbon monoxide.



In summary, therefore, all of the volatile products and separate features of degradation can be rationalised by a reaction initiated by random back-bone bond scission followed by a chain of free radical transfer reactions both inter- and intramolecular with competing free radical side reactions involving the polymer radical formed during these transfer processes.

The results of the degradation experiments on PMA carried out in this present work, althoughmainly qualitative, seem to substantiate previous findings. Major degradation products were found to be mainly chain fragments collected at the 'cold ring', with carbon dioxide and methanol the main condensable volatile products. Although no quantitative work was done, methanol was found to be formed in greater quantities than carbon dioxide, with methyl acrylate production possibly greater than that proposed by Straus and Madorsky[52] or Cameron and Kane.[57] Actual quantities may be closer to the values found by Chitoku and Baba[68] employing a degradation programmed to 400°C at 2.5°C/min.

The production of the small molecular volatiles such as methanol and carbon dioxide explain the separation of the -196°C. -100°C and -75°C traces in the TVA (Figure 4.4). The very small difference in the -75°C, -45°C and 0°C traces is indicative of the small amount of chain fragments and MMA which reach these traps. The TVA trace also confirms the production of non-condensable species concurrent with the main degradation process. This is due to the formation of hydrogen and carbon monoxide, the loss of the former leading to conjugated sequences in the residue and thus accounting for the development of colouration.

Evidence from TVA, TG and DSC curves show that degradation is a one-stage process and that this, in addition to the nature and quantities of degradation products, may be most satisfactorily accounted for in terms of the mechanisms previously described.

CHAPTER 5

THERMAL DEGRADATION OF 2-BROMOETHYL METHACRYLATE AND METHYL ACRYLATE COPOLYMERS

5.1 INTRODUCTION

Four copolymers of 2BEM-MA were prepared by the method outlined in Chapter 2, and their compositions determined by the Nuclear Magnetic Resonance Spectroscopic technique described in Chapter 3. The composition of the copolymers covered the whole range with 81% (A1), 69% (A2), 48% (A3) and 9% (A4) of 2BEM units, having average molecular weights of 41.5×10^4, 22.2×10^4, 15.4×10^4 and 8.1×10^4, respectively. As the MA content increases the average molecular weight decreases, possibly due to the increasing importance of transfer reactions involving MA terminal radicals during polymerisation.

It was observed that as the MA content increased, the polymer became softer and more tacky and consequently more difficult to handle. Copolymers A1 and A2 were powders, copolymer A4 was soft and tacky, with copolymer A3 having

intermediate properties. For thermal analysis copolymers A3 and A4 were cut into very small pieces to simulate a powder.

The above compositions are quoted as a number percentage of 2BEM units. However, as the monomer unit of 2BEM is over twice as heavy as the MA unit, the corresponding weight percentage of each monomer will have different values. This bias should be considered when relating production of volatiles to copolymer composition as well as to weight loss studies.

In the following section it has sometimes been advantageous to include results from both homopolymer systems together with those for the copolymers for comparative purposes.

5.2 THERMAL ANALYSIS

(i) Thermogravimetry

The weight loss curves for the four copolymers together with those for the respective homopolymers are shown in Figure 5.1. The first and most obvious feature is that all the copolymers are relatively more stable than P2BEM but less stable than PMA, the stability increasing with MA content.

None of the copolymers, even copolymer A1 containing 81% of 2BEM units, exhibits a low temperature weight loss which was a feature of P2BEM homopolymer and attributed to chain-end initiated depolymerisation. Each copolymer begins to volatilise at just over 300°C displaying a two stage process, the relative importance of each stage being dependent on the copolymer composition. Copolymer A2 (69% 2BEM) for example has lost 80% of the original weight by 380°C, whereas copolymer A4 (9% 2BEM)

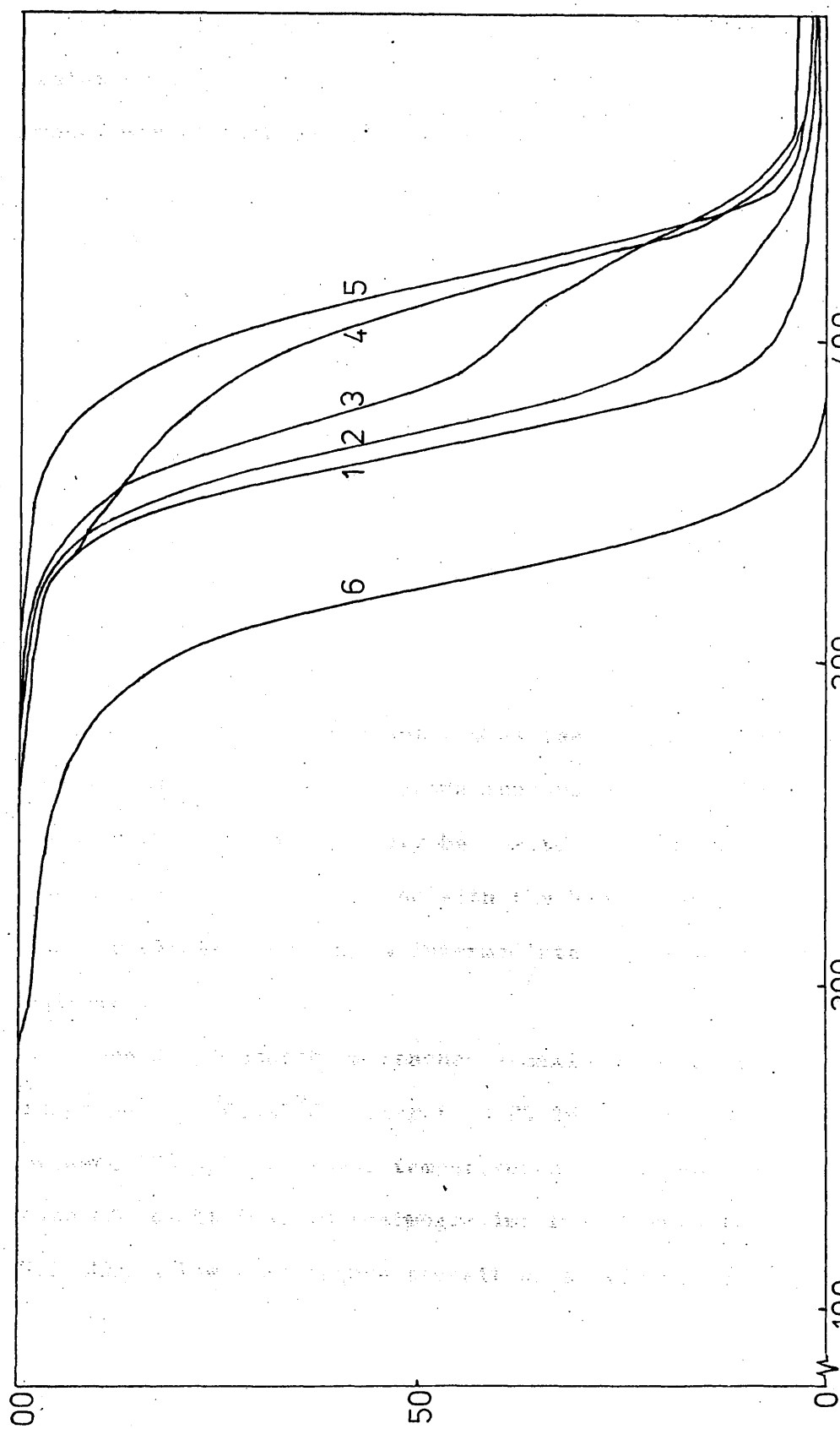


FIGURE 5.1 TG CURVES OF COPOLYMERS 2BEM-MA AND RESPECTIVE HOMOPOLYMERS

1: A1 (81% 2BEM), 2: A2 (69% 2BEM) 3: A3 (48% 2BEM), 4: A4 (9% 2BEM), 5: PMA, 6: P2BEM

has lost only 20% after that first stage. The first stage reaches a maximum rate of weight loss in the temperature range 348-369°C with the second stage in the range 405-426°C. The weight loss in the first stage closely corresponds to the relative weight of the 2BEM in the copolymer. For example copolymer A3 with 48% 2BEM units making up approximately 68% of the original weight shows (curve 3, Figure 5.1) almost 70% weight loss after the first stage is completed.

The residue from all of the copolymers at 500°C accounts for only a few per cent of the original sample weight.

(ii) Differential Scanning Calorimetry

The DSC curves for the four copolymers as well as those for the respective homopolymers are illustrated in Figure 5.2. This representation clearly shows two endotherms, the relative importance of each being dependent upon copolymer composition.

Copolymer A3 (Curve 4) which approximates to a 1:1 composition shows a greater endotherm at lower temperature. This suggests that the major degradation processes occur at lower temperature and may possibly be due to interaction of two monomeric units. Comparison with the homopolymer curves shows that copolymer behaviour is intermediate to the homopolymer extremes.

The first endotherm reaches a maximum in the temperature range 344-360°C, 25°C higher than P2BEM, the second occurs between 408-425°C. These temperatures correspond to maximum rate of weight loss in thermogravimetry. Curves 1-4 in Figure 5.2 show a low temperature transition attributable to the glass

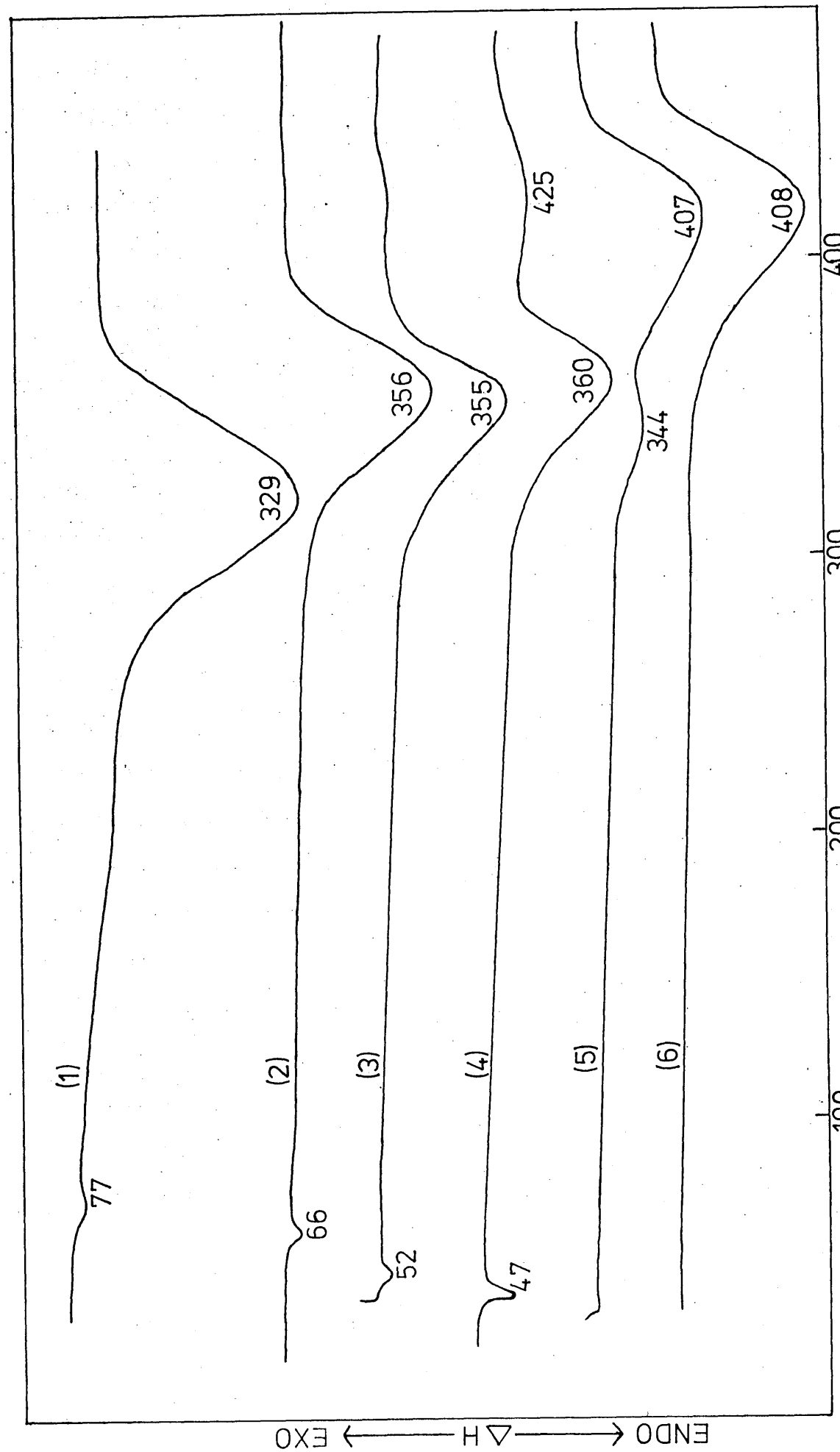


FIGURE 5.2 DSC CURVES FOR (1) P2BEM (2) A1 (3) A2 (4) A3 (5) A4 and (6) PMA.

transition temperature. As the MA content in the copolymers increases, the glass transition temperatures decrease to a minimum value of 5°C for PMA homopolymer.[69]

(iii) Thermal Volatilisation Analysis

The copolymers were examined in powder form with sample sizes 50-60mg. They were heated to 500°C at 10°C/min under normal TVA conditions. The other features of TVA, namely the 'cold ring' fraction and residue will be described in addition to a detailed account of the volatilisation thermograms.

The TVA traces for copolymers A1, A2, A3 and A4 are shown in Figures 5.3, 5.4, 5.5 and 5.6 respectively. As in TG and DSC, the most striking feature is the two stage volatilisation profile, the relative size of the peaks changing with copolymer composition.

At approximately a 1:1 monomer composition (Figure 5.5) the lower temperature peak predominates, substantiating information from thermogravimetry and DSC. Volatilisation for all the copolymers begins at just over 300°C. Copolymers A1 and A2, which have a high 2BEM content, show now low temperature shoulder on the first peak attributed to chain-end initiated depolymerisation in P2BEM homopolymer.

The Tmax of the first peak occurs at approximately 360°C with T'max of the second stage in the region of 415°C. These values correspond closely to those of maximum weight loss from thermogravimetry and maximum heat input in DSC. Thus, the degradation processes giving rise to weight loss, endothermic heat transfer and volatilisation occur concurrently.

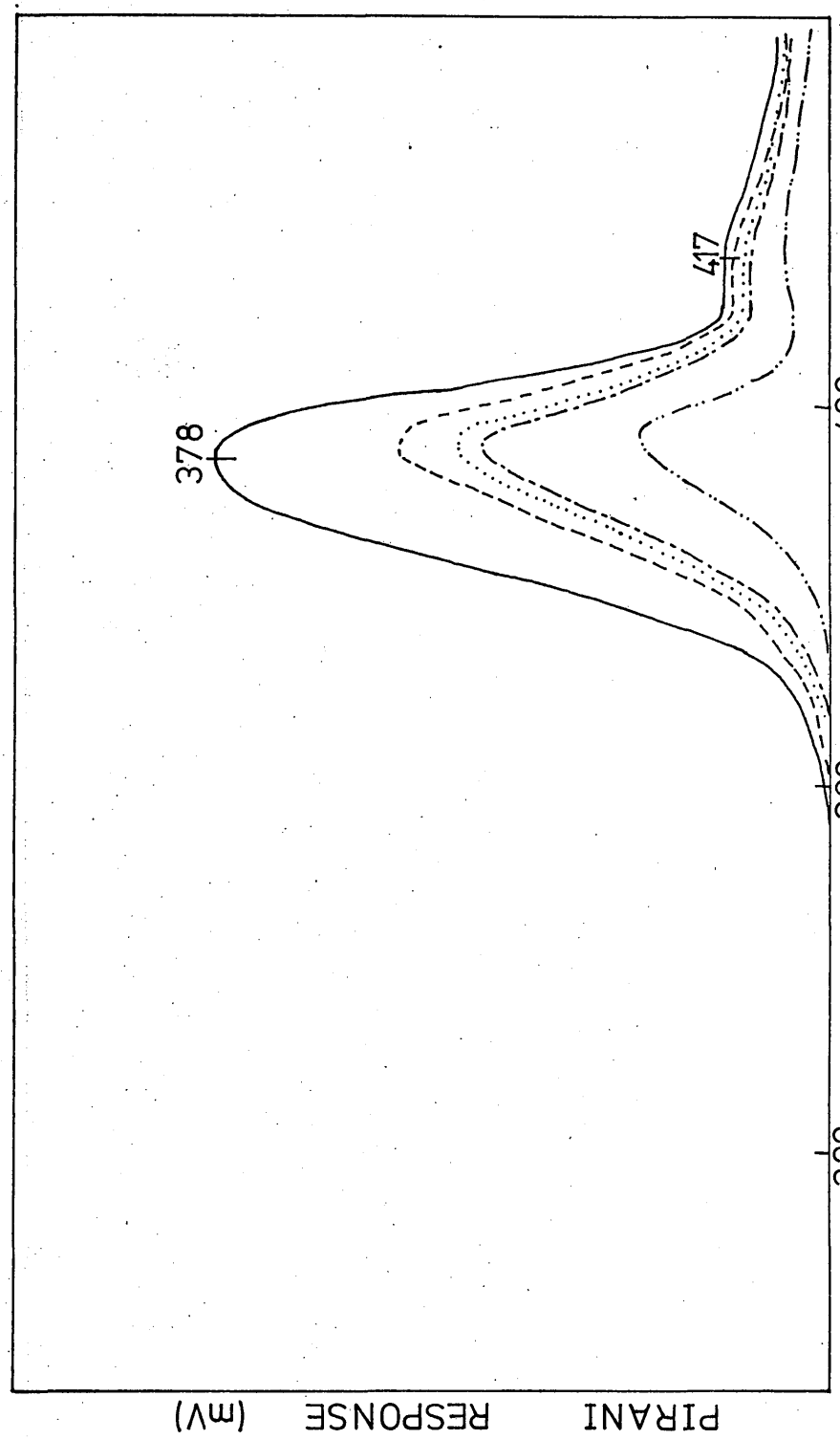


FIGURE 5.3 TVA TRACE OF COPOLYMER A1 (81% 2BEM), 53.4 mg POWDER AT 10°/min.

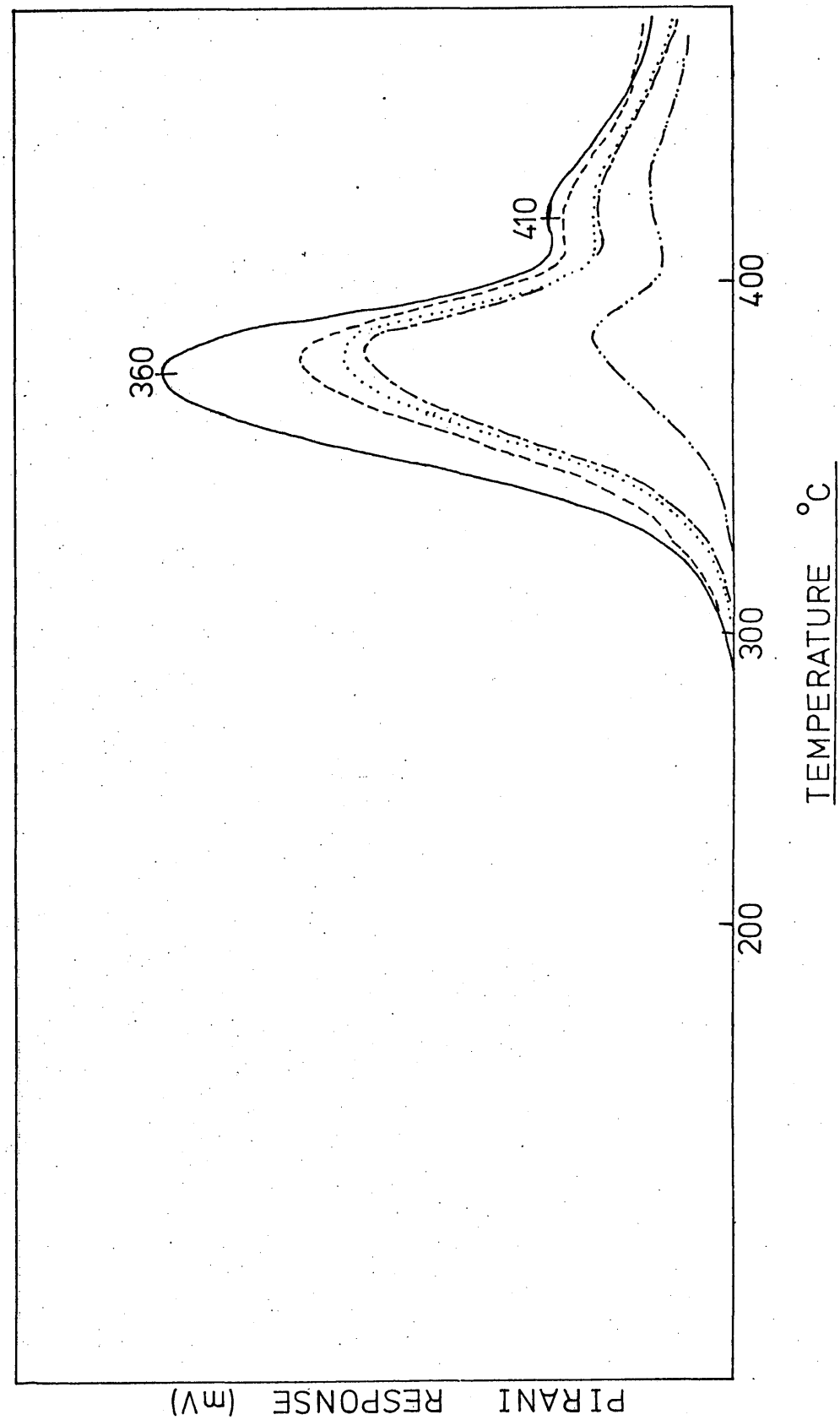


FIGURE 5.4 TVA OF COPOLYMER A2 (69% 2BEM) 60 mg POWDER AT 10°/min.

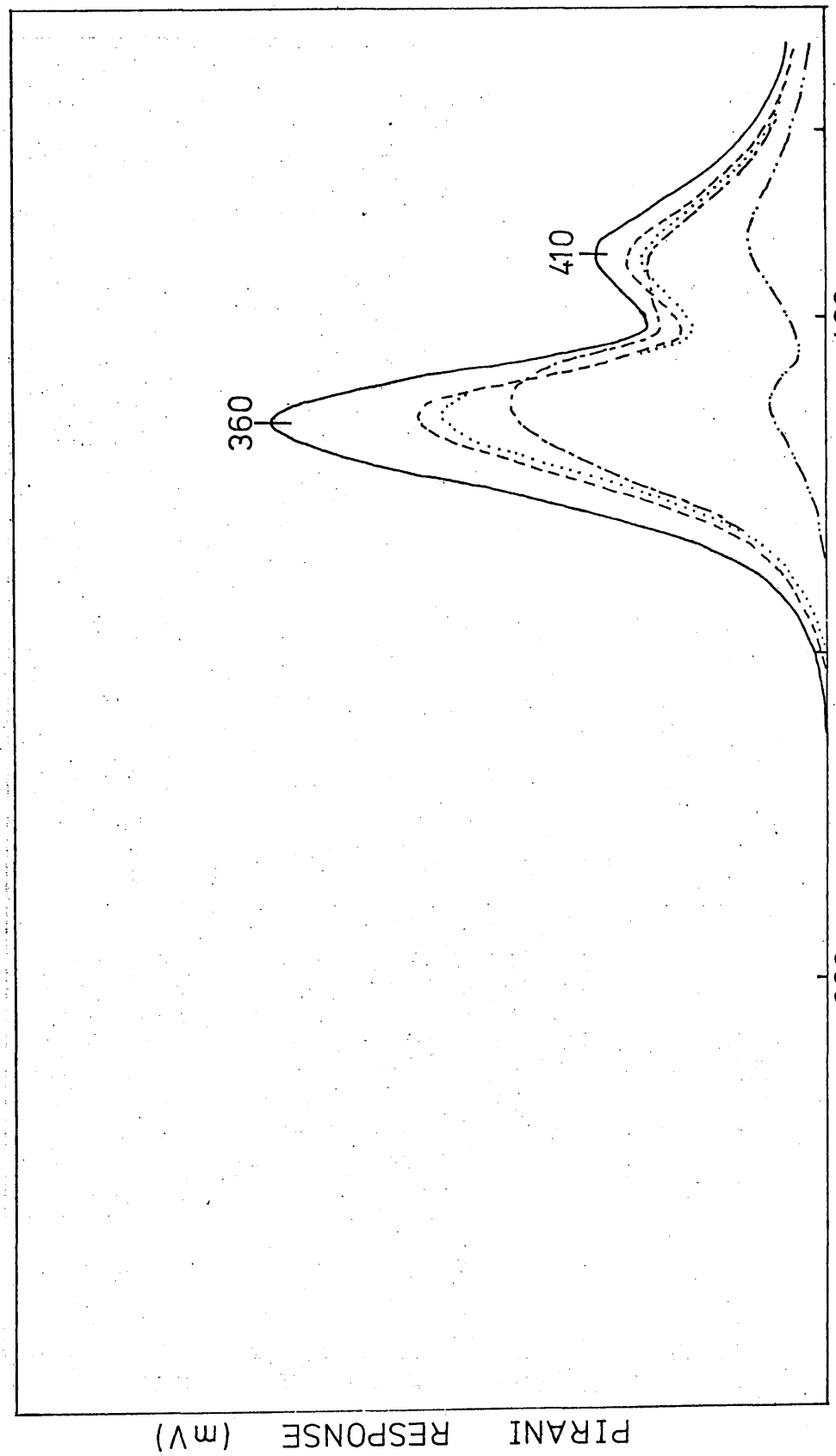


FIGURE 5.5 TVA OF COPOLYMER A3 (48% 2BEM) 60 mg THIN FILM AT 10°/min.

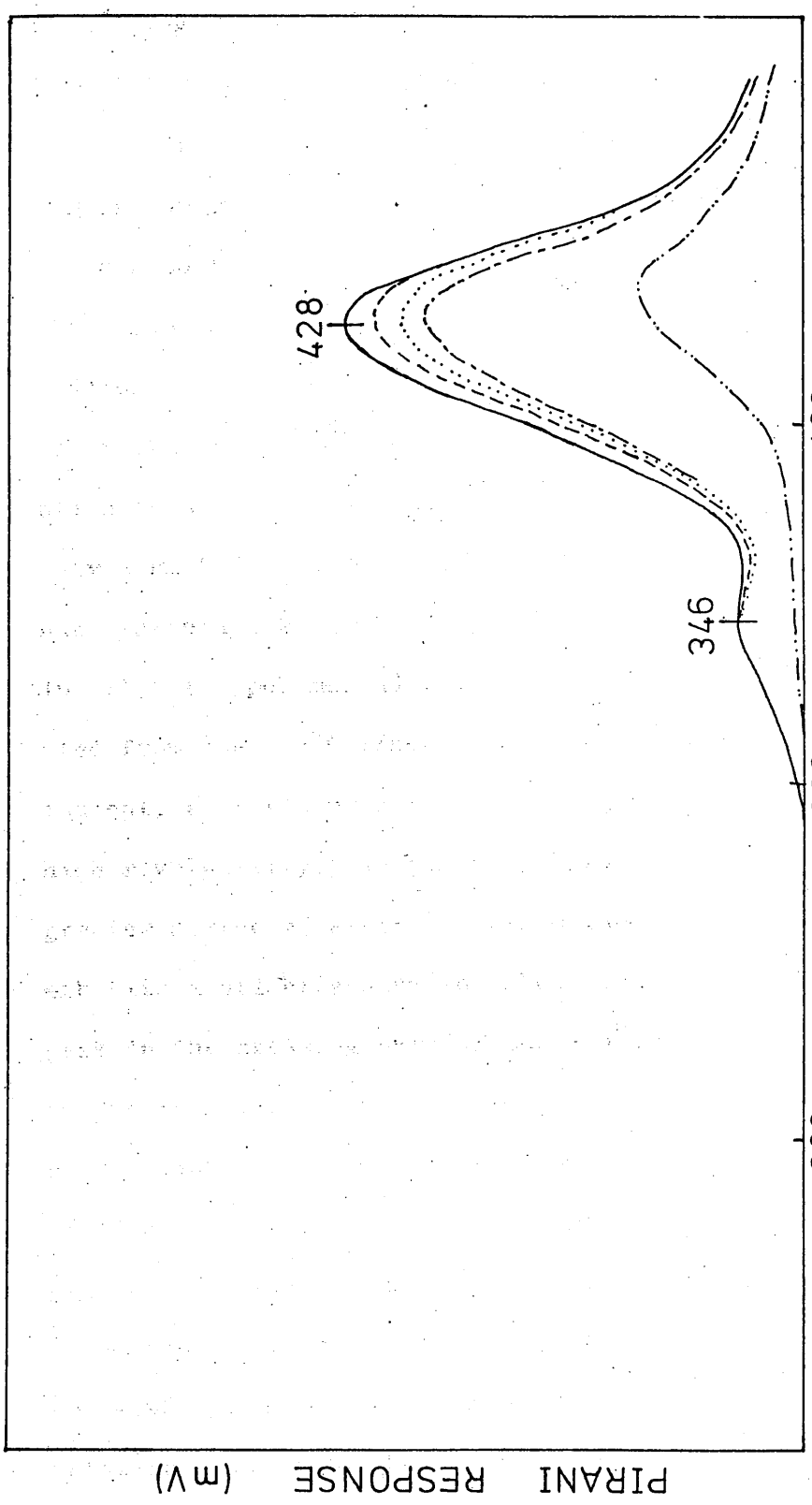


FIGURE 5.6 TVA TRACE OF COPOLYMER A4 (9% 2BEM) 53.4 mg THIN FILM AT 10°/min.

In each thermogram the traces from the various traps are separated to some extent. The TVA traces from copolymers containing a high percentage of 2BEM monomeric units (Figures 5.3, 5.4 and 5.5) show a separation of the $0^{o}C$ and $-45^{o}C$ traces. This separation is indicative of a high boiling product. This feature of the degradation of P2BEM homopolymer (Figure 4.1) was due to the production of 2BEM monomer. The remaining copolymer which contains 9% of 2BEM units, however, exhibits minimal separation of these traces. The $-45^{o}C$ and $-75^{o}C$ traces in all the thermograms were virtually co-incident, with maximum separation occurring at peak maxima. This near coincidence means that only a small amount of degradation products are formed which can pass through the $-45^{o}C$ trap but are condensed in the $-75^{o}C$ trap. In all but copolymer A3 (Figure 5.5) the $-100^{o}C$ trace is separated from the $-75^{o}C$ trace to a small extent. Again, this is indicative of the production of a small amount of species with higher volatility. In Figure 5.5 the $-100^{o}C$ trace shows a greater degree of separation from the $-75^{o}C$ trace. It also exhibits a slightly anomalous behaviour just after the first peak in the crossing over of the $-45^{o}C$ and $-75^{o}C$ traces. This is due to a limiting rate effect, where distillation of some product in a low temperature trap occurs to that of the trap at liquid nitrogen temperature, causing an increase in the pressure measured by the Pirani gauge behind the respective trap.

Each thermogram displays a large separation of the $-100^{o}C$ and $-196^{o}C$ traces. This is due to the formation of relatively volatile small molecular species which pass through the $-100^{o}C$ trap but can be condensed at liquid nitrogen temperature under

the vacuum conditions. This substantial separation implies that these species constitute a major part of the reaction products.

The formation of non-condensable products occurs during both stages for each copolymer and follows the general profile of volatilisation. Initial formation of these products commences at about 330°C in each copolymer system and continues until 500°C. Comparison with each homopolymer shows that this initial temperature is approximately 50°C lower than for PMA (Figure 4.4) homopolymer, while P2BEM homopolymer produces no non-condensables. The outline of the -196°C trace mirrors that of volatilisation in Figures 5.3, 5.4 and 5.6. However, in Figure 5.5 the second stage of volatilisation produces a greater amount of non-condensable products than the first, the reverse of the total volatilisation profile.

At high methacrylate content the first stage of degradation is characterised by significant formation of a high boiling fraction concurrent with the production of various volatiles including non-condensable species. On the other hand, at high methyl acrylate content, this first stage of volatilisation becomes less important with the production of this high boiling fraction greatily diminished and the formation of more volatile species predominating.

The degradation products responsible for the general outline of these thermograms were identified by various analytical techniques and will be discussed in detail later.

The amount of 'cold ring' fraction produced after each TVA experiment not only increased, but also the colouration of this

fraction intensified as the methyl acrylate content increased. This fraction was soluble in carbon tetrachloride, and was analysed by solution infra-red, ultra-violet and NMR spectroscopy.

After each TVA experiment of the copolymer systems, only a very small amount of black residue remained on the bottom of the degradation tube. Analysis of the residue at various stages of degradation was carried out by monitoring the infra-red spectrum of a thin film of polymer cast from solution on a salt plate.

5.3 ANALYSIS OF PRODUCTS FROM THERMAL DEGRADATION

The various fractions of degradation products were investigated by a number of analytical and spectroscopic techniques. In order to characterise each product completely a number of degradations had to be carried out to confirm reproducibility of results. Quantitative measurements of a number of condensable products have been made and will be presented later. However, a qualitative picture of the nature of products evolved at each stage of degradation will contribute to an overall understanding of the decomposition processes. Each stage of degradation will be discussed in some detail in the following section.

5.3 (a) QUALITATIVE ANALYSIS OF PRODUCTS FROM DEGRADATION TO 500°C

(i) Condensable Products

Qualitative analysis of the condensable products from degradation to 500°C was carried out by employing gas phase or liquid infra-red spectroscopy and mass spectrometry. The sub-ambient TVA technique described in Chapter 2 was used to aid

separation of the condensable products before subsequent analysis by the above spectroscopic methods. Application of this separation technique reduces the possibility of any minor species being masked in the infra-red spectrum by a more abundant product. It may also be used in isothermal degradations by aiding identifications of products from various stages of reaction, and to give a semi-quantitative picture of the nature and amounts of individual products formed at each stage of degradation.

The gaseous infra-red spectrum of the condensable volatiles from differential condensation TVA for copolymer A3 is shown in Figure 5.7. This spectrum is representative of all the copolymer systems studied, the various amounts of each product being a function of the composition of the copolymer. The volatiles were identified by comparison with the respective reference spectra and the assignment of the peaks are summarised in Table 5.1. The distillate which was liquid at room temperature was analysed by infra-red spectroscopy in the form of a thin film and identified as pure 2BEM monomer.

A more detailed analysis of all the condensable products was achieved by employing the sub-ambient TVA technique after programmed degradation to 500^{o}C. Such a trace for copolymer A3 is shown in Figure 5.8. The more volatile species could be identified by gas phase infra-red spectroscopy. However, as the volatility of the products decreased this method became less useful. Analysis of the higher boiling products was carried out by liquid phase infra-red spectroscopy, or more commonly by the

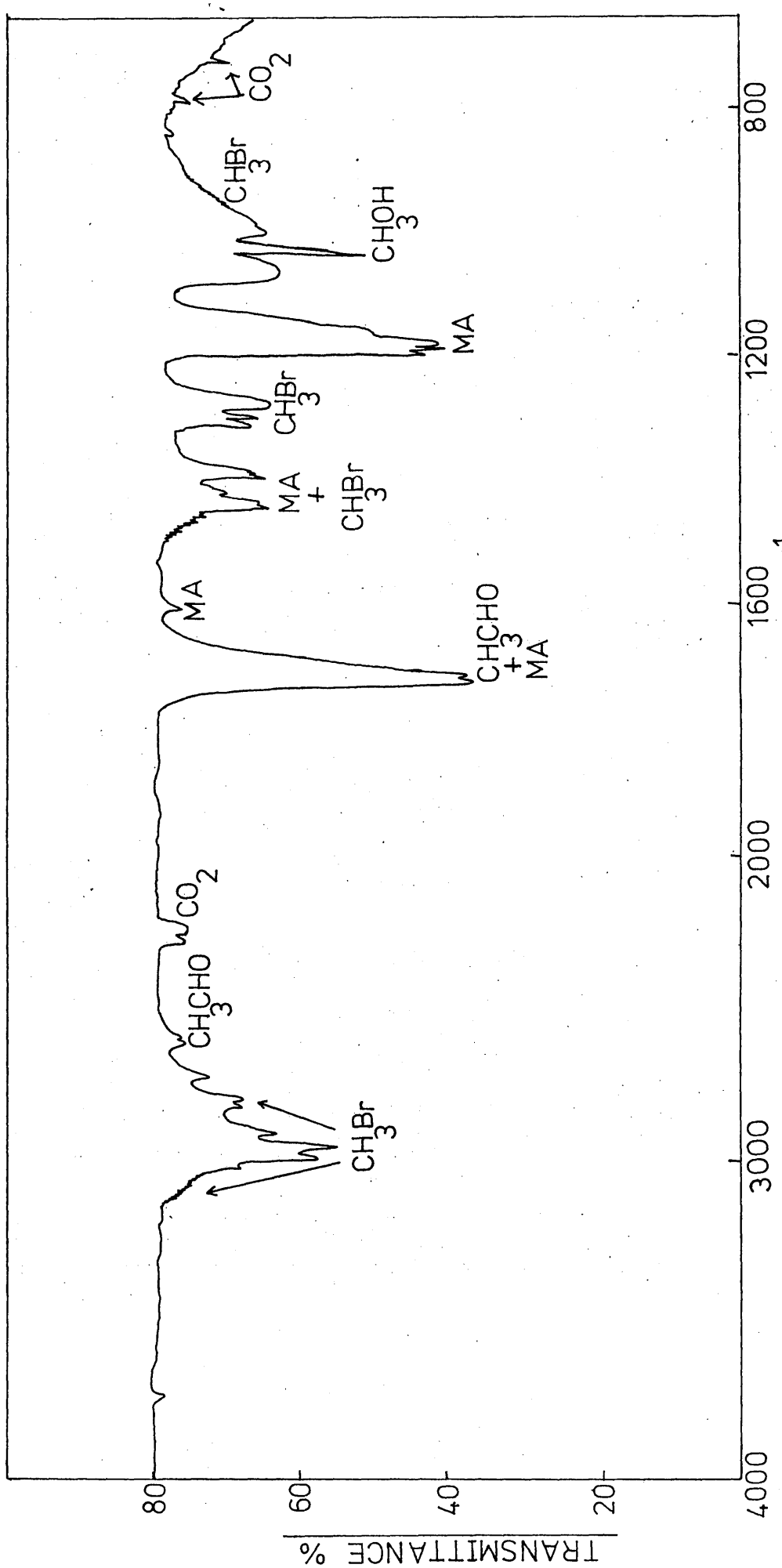


FIGURE 5.7 GAS PHASE IR SPECTRUM OF CONDENSABLE VOLATILES FROM TVA OF COPOLYMERS A3 (48% 2BEM) TO 500°C.

TABLE 5.1

ASSIGNMENT OF IR PEAKS OF

DEGRADATION PRODUCTS OF COPOLYMER A3

FREQUENCY CM^{-1}	MODE	COMPOUND OR GROUP
3700	O-H STRETCHING	CH_3OH
3120-3000 Rotational Fine Structure	C-H STRETCHING	CH_3Br
2980-2840	"	CH_3Br
2720-2700	" (Doublet)	CH_3CHO
2340-2300	C=O STRETCH	CO_2
1760-1748	C=O STRETCH (Doublet)	CH_3CHO + $CH_2{=}CHCO_2CH_3$
1630	C=C STRETCH	$CH_2{=}CHCO_2CH_3$
1500-1350	CH_3 SYMMETRICAL DEFORMATION (Fine Structure)	CH_3Br
1450)) 1410)	C-H DEFORMATION	$CH_2{=}CHCO_2CH_3$
1320-1280	C-Br STRETCH (Triplet)	CH_3Br
1200	C-O STRETCH	$CH_2{=}CHCO_2CH_3$
1060-1000	C-O STRETCH (Triplet)	CH_3OH
1000-900	C-H DEFORMATION (Fine Structure)	CH_3Br
721	C-O BEND	CO_2
667	C-O BEND	CO_2

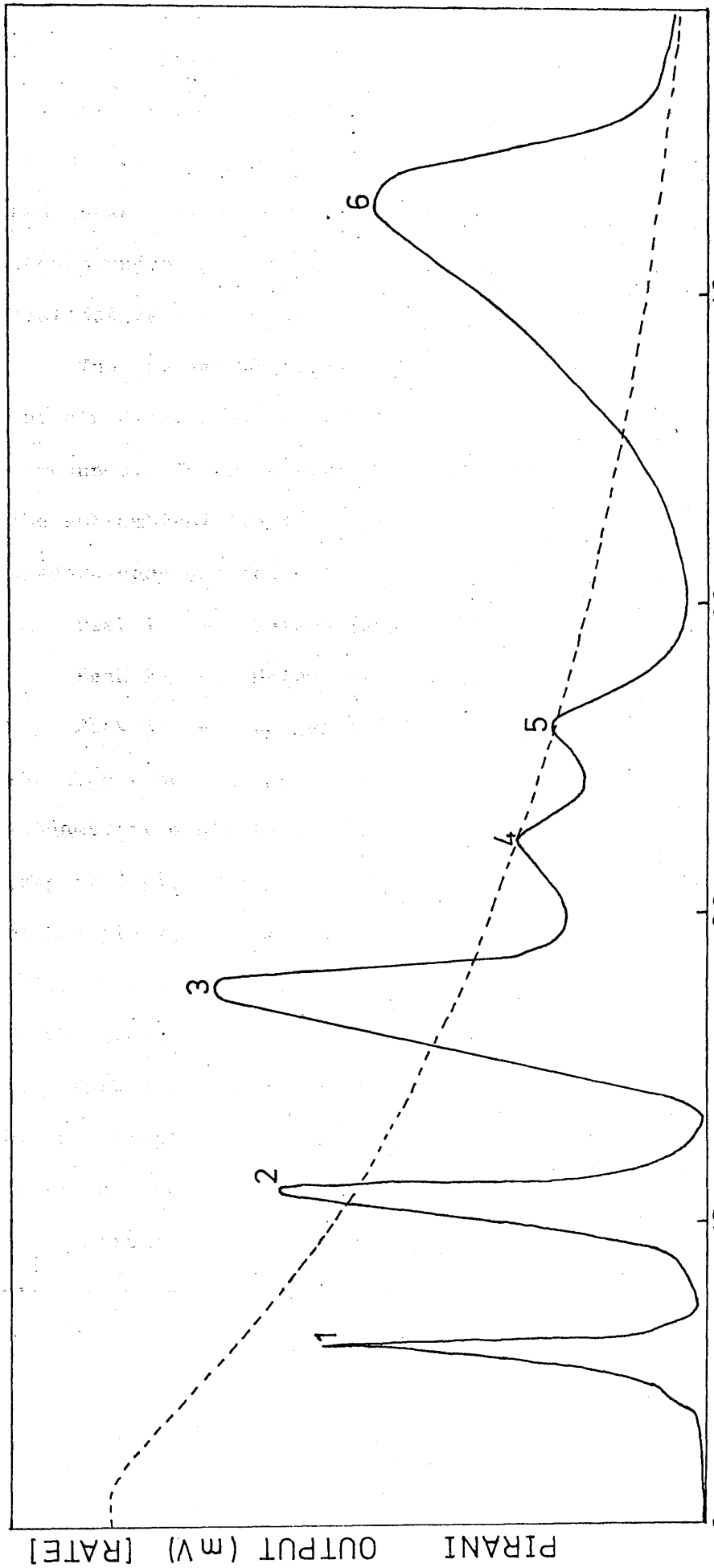


FIGURE 5.8 SUB AMBIENT TVA TRACE OF COPOLYMER A3. VOLATILES FROM DEGRADATION TO 500°C.

more sensitive technique of mass spectrometry. The latter method proved to be particularly useful during these studies, by aiding the identification of brominated species in the degradation products. The bromine atom has two isotopes of roughly equal natural abundance (^{79}Br 50.52%, ^{81}Br 49.48%) and appears as a doublet, spaced two mass units apart. If a compound or mass fragment contains two bromine atoms a very distinctive 1:2:1 triplet is observed.

The sub-ambient peaks were assigned by comparison of infra-red and massspectra with spectra from a number of reference compounds. The products which made up the first three peaks in the sub-ambient TVA trace were identified by gas phase infra-red spectroscopy and found to be :-

Peak 1 - Ketene (minor) and Carbon Dioxide

Peak 2 - Methyl Bromide andsome Acetaldehyde

Peak 3 - Methyl Acrylate and some Methanol

The higher boiling products which make up peaks 4 and 5 in the sub-ambient distillation trace were analysed by mass spectrometry (Figure 5.9). The reference spectra of 1,2, dibromoethane, methyl methacrylate, 2 bromoethanol and ethyl methacrylate are also illustrated. Comparison of the spectra confirms the presence of these compounds among the degradation products.

Peak 6 in the sub-ambient trace was found to be 2BEM monomer by mass spectrometric analysis, in conjunction with liquid phase infra-red spectroscopy.

Table 5.2 summarises the condensable products identified with a semi-quantitative assignment for this particular copolymer

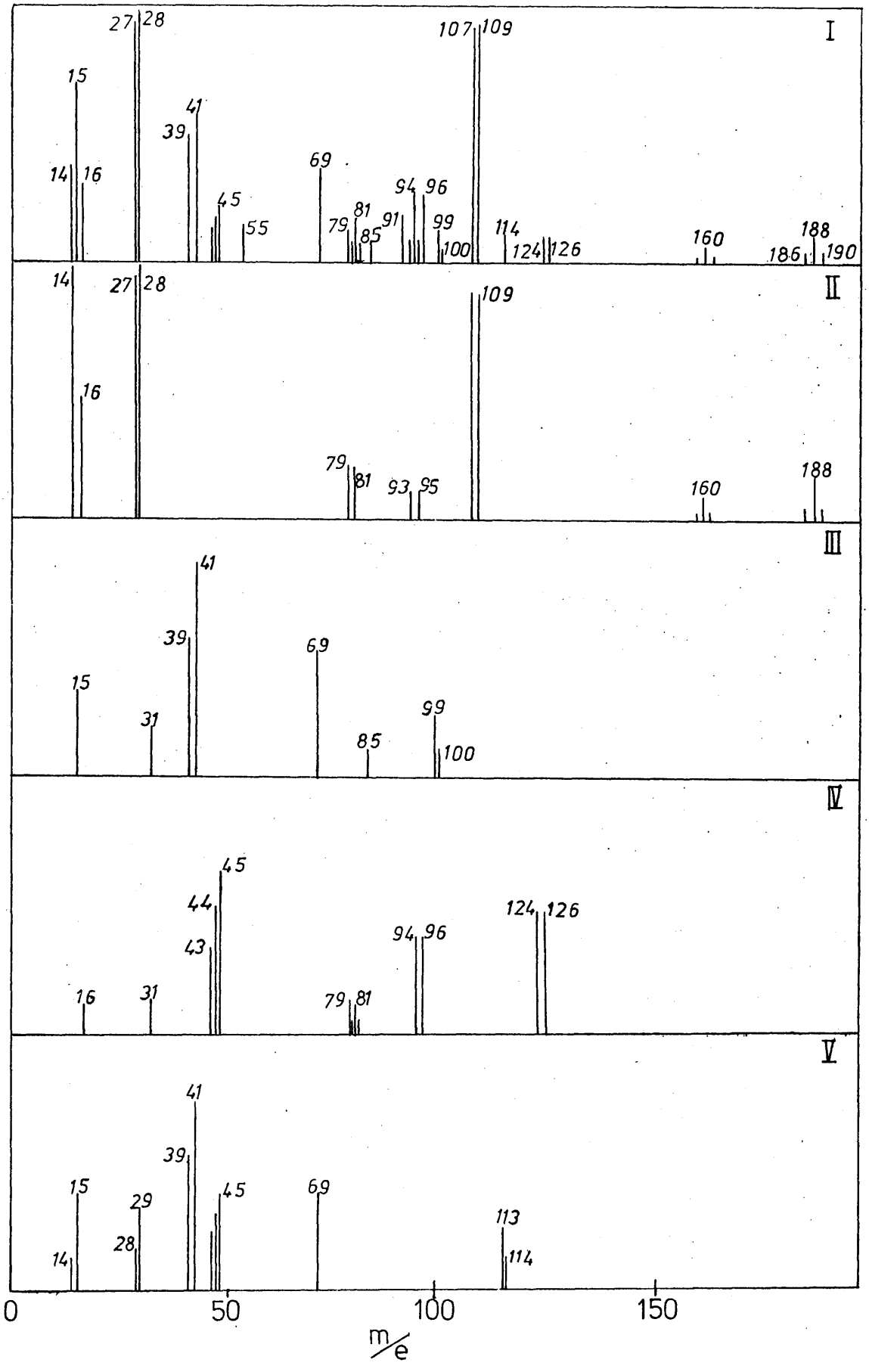


FIGURE 5.9 MASS SPECTRA OF I - FRACTIONS 4 & 5 FROM SUB-AMBIENT TVA TRACE OF A3 DEGRADED TO 500°C II - 12 DIBROMOETHANE III - METHYL METHACRYLATE IV - 2 BROMOETHANOL V - ETHYL METHACRYLATE.

TABLE 5.2

QUALITATIVE ANALYSIS OF PRODUCTS FROM DEGRADATION OF COPOLYMER A3 TO 500°C

PRODUCT	QUANTITY	MODE OF ANALYSIS
CARBON DIOXIDE	MAJOR	I.R. (GAS PHASE) & MASS SPECTROMETRY
METHYL BROMIDE	MAJOR	"
METHYL ACRYLATE	MAJOR	"
2-BROMOETHYL METHACRYLATE	MAJOR	I.R. (LIQUID PHASE) & MASS SPECTROMETRY
ACETALDEHYDE	MAJOR	I.R. (GAS PHASE)
1,2,DIBROMOETHANE	MEDIUM	MASS SPECTROMETRY
METHANOL	MEDIUM	I.R. (GAS PHASE)
METHYL METHACRYLATE	MEDIUM	I.R. (GAS PHASE) & MASS SPECTROMETRY
VINYL BROMIDE	MINOR	I.R. (GAS PHASE) & MASS SPECTROMETRY
HYDROGEN BROMIDE	TRACE	I.R. (GAS PHASE)
KETENE	TRACE	I.R. (GAS PHASE)
BROMOETHANOL	TRACE	MASS SPECTROMETRY
ETHYL METHACRYLATE	TRACE	MASS SPECTROMETRY

system, as well as the mode of analysis. Four of the products identified, namely methyl bromide, 1,2 dibromethane, acetaldehyde and methyl methacrylate were of particular interest. The first three are not found among the degradation products of either of the homopolymers. MMA, however, is found to be a minor product from PMA. In this study MMA is formed in greater quantities than could be expected from the equivalent amount of MA in the copolymer. Most of the other minor or trace products may be explained by the fragmentation of the respective monomer units. Since they do not occur in substantial amounts their formation may be evidence of competing side reactions involving intermediates produced during the major degradation processes.

(ii) Non-condensable Products

These products were investigated by carrying out degradations in a closed system. They were transferred to the infra-red cell by means of a Toeppler pump. Methane and carbon monoxide were identified by this method and hydrogen was detected by mass spectrometric analysis.

(iii)'Cold Ring' Fraction

The amount and intensity of colour of this yellow coloured fraction was found to increase as the MA content of the copolymer increased. It was examined by infra-red, ultra-violet and NMR spectroscopy as a solution in CCl_4.

(a) Infra-red Analysis

Figure 5.10 shows the spectra of the undegraded polymer sample ($CHCl_3$) and of the 'cold ring' fraction (CCl_4) obtained after degradation of copolymer A2 to 500°C. They are similar

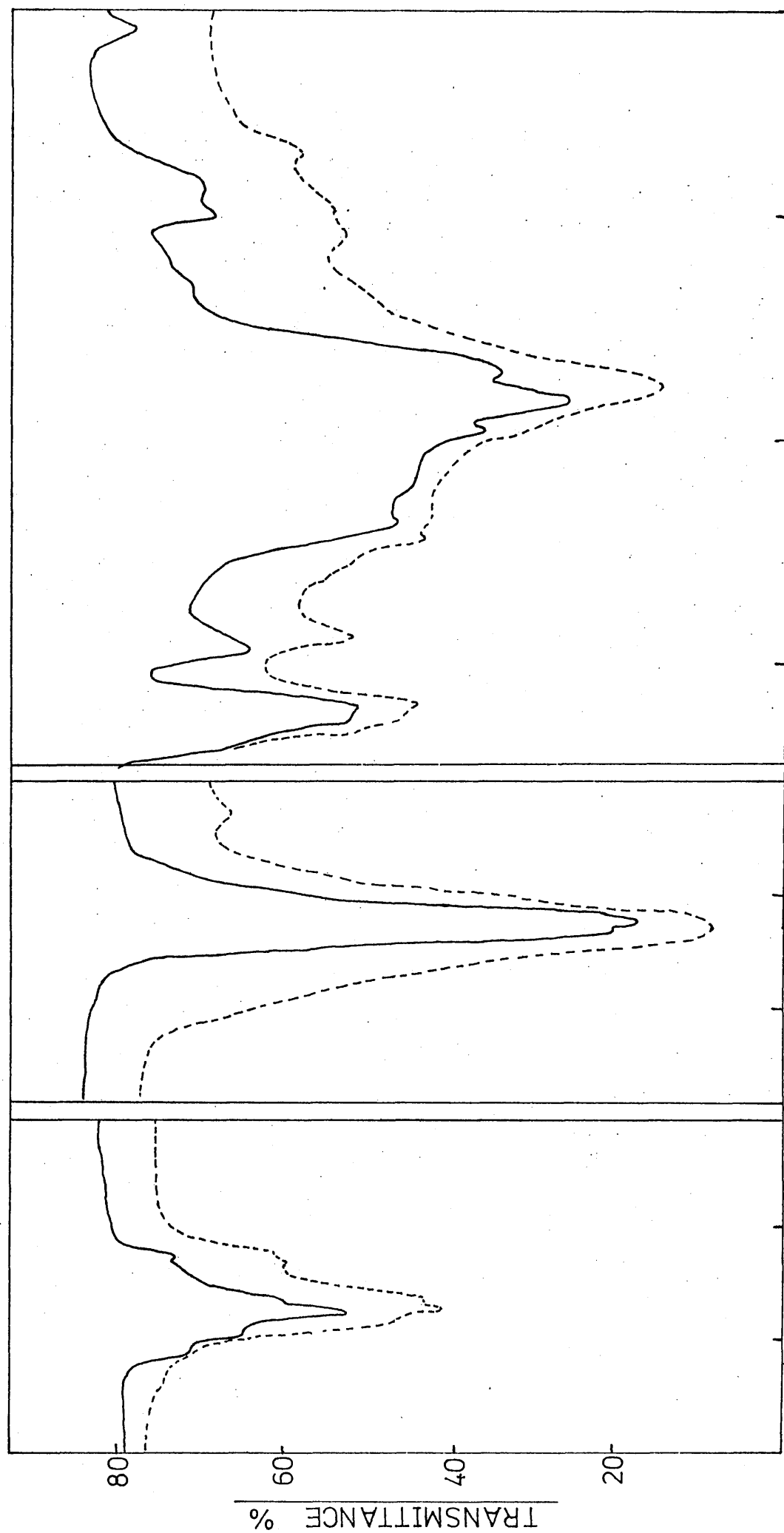


FIGURE 5.10 INFRA-RED SPECTRA OF I - UNDEGRADED COPOLYMER A2 ($CHCl_3$ SOLVENT) II - COLD RING FRACTION FROM DEGRADATION TO 500°C OF COPOLYMER A2 (CCl_4 SOLVENT).

in certain respects but there are several significant differences. There is a slight increase in absorption in the unsaturated carbon-hydrogen stretching region above 3000cm^{-1} in the spectrum of the 'cold ring' fraction. There also appears to be a general broadening of the carbonyl region of the CRF to both higher and lower frequencies. The actual carbonyl peak apparently shifts from 1725cm^{-1} in the original sample to 1745cm^{-1} in the degradation fraction.

A new absorption at 1630cm^{-1} is formed in spectrum II which is attributable to the carbon-carbon double bond stretching mode.

Comparison of the fingerprint region shows a number of differences not only in peak intensities but also in actual absorption frequencies. The broad carbon-oxygen stretching region shows a marked change even allowing for distortion due to solvent absorption ($CHCl_3$). The carbon-oxygen stretching region changes from a rather complex set of peaks in the original undegraded sample to a single peak at 1150cm^{-1} in the 'cold ring' fraction.

In order to observe changes in the carbon-bromine bond stretching region which occurs below 625cm^{-1}, potassium bromide cells which do not begin to absorb radiation until 400cm^{-1} were employed. Both the spectra of the original sample (KBr disc) and the 'cold ring' fraction of copolymer A3 (CCl_4 solution) are shown in Figure 5.11. Peaks at 682cm^{-1}, and 573cm^{-1} clearly indicate the existence of primary carbon-bromine bonds in the 'cold ring' fraction, although the shift in absorption frequencies suggests slight structural modifications.

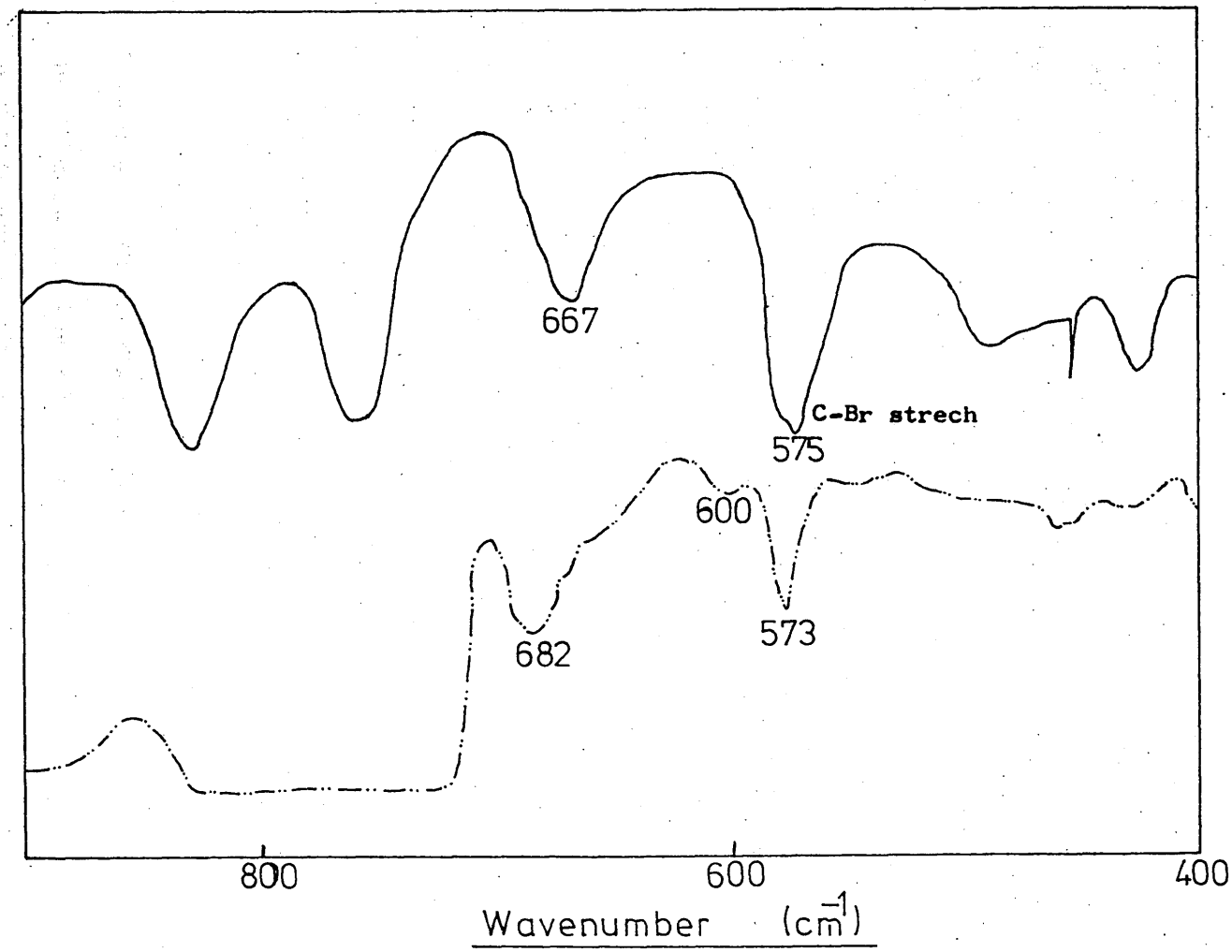


FIGURE 5.11 INFRA-RED SPECTRUM TO 400°cm^{-1} OF (I) UNDEGRADED SAMPLE OF COPOLYMER A3 (KBr DISC) (II) COLD RING FRACTION FROM TVA TO 500°C (CCl_4 SOLUTION).

(b) Ultra-violet Spectroscopy

The ultra-violet spectra of this fraction from each of the copolymers shows an increase in absorption in the 2750-3550Å region as illustrated in Figure 5.12. Table 5.3 shows the colour to be expected from various lengths of carbon-carbon conjugation which suggests that conjugated sequences up to six units in length are present in the coloured material. This confirms the appearance of ethylenic structures observed by the absorption at 1630cm^{-1} in the infra-red spectrum of this fraction.

Table 5.3 Colour and Absorption Maxima for Conjugated Ethylenic Structures

Length of Conjugation	Colour	Absorption Maxima Å
4	Pale Yellow	2960
5	Pale Yellow	3350
6	Yellow	3600
8	Orange	4150

The fact that the colour of the CRF intensifies with increasing methyl acrylate content suggests that the length of conjugated sequences increases with methyl acrylate content.

(c) Nuclear Magnetic Resonance Spectroscopy

The NMR spectra for both the original copolymer and 'cold ring' fraction are shown in Figure 5.13. Peak B in spectrum I is due to the combined absorption of the -OC$\underline{H}_3$ protons of the MA unit and the -C$\underline{H}_2$—Br protons of the methacrylate unit. Peak A is due solely to the -OC$\underline{H}_2$— protons of the methacrylate unit. Spectrum II shows an inversion of the relative intensities

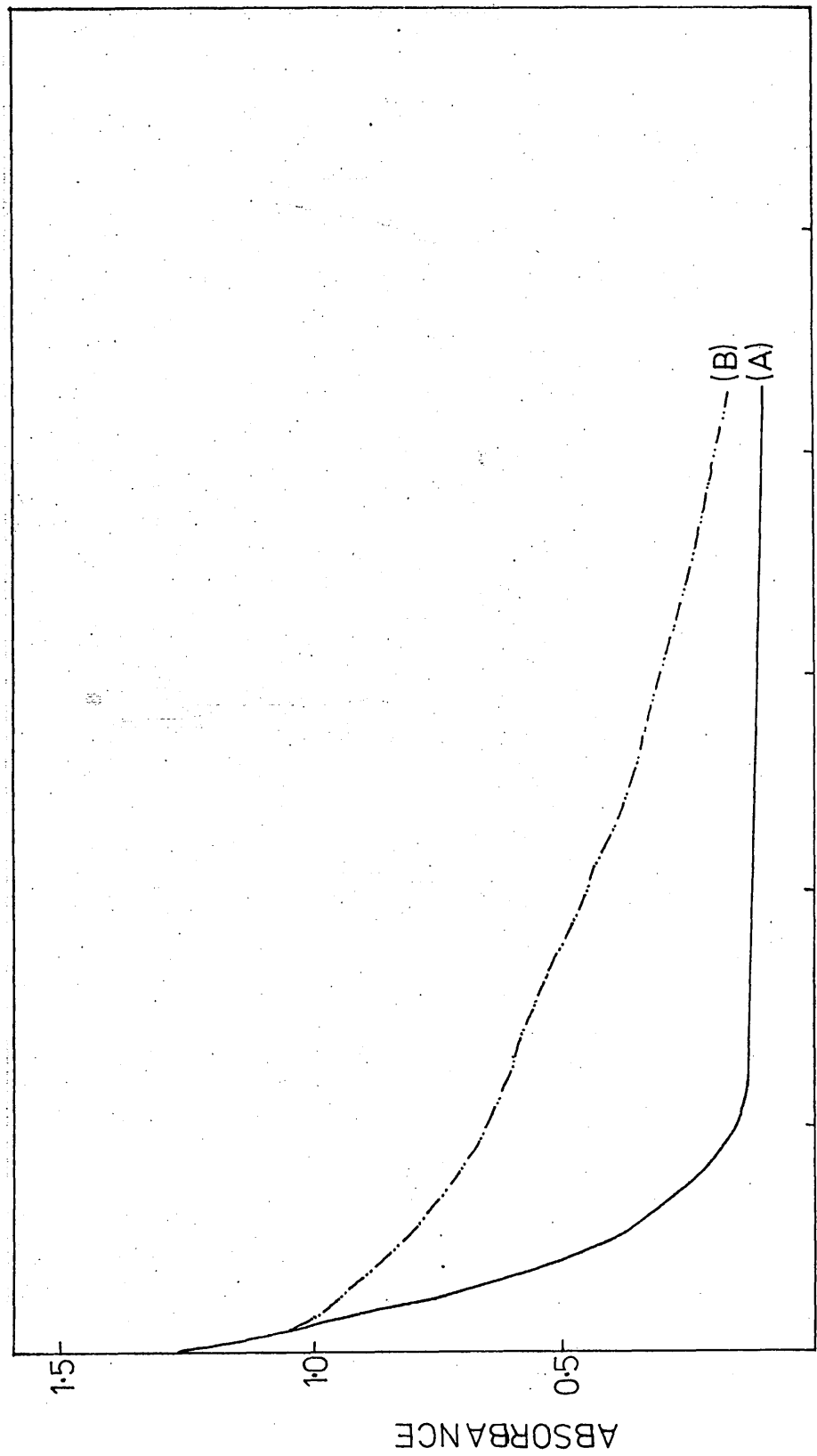


FIGURE 5.12 ULTRA VIOLET ABSORPTION SPECTRA OF COPOLYMER A3 (48% 2BEM) (A) UNDEGRADED POLYMER (B) COLD RING FRACTION (IN CCl_4 SOLUTION).

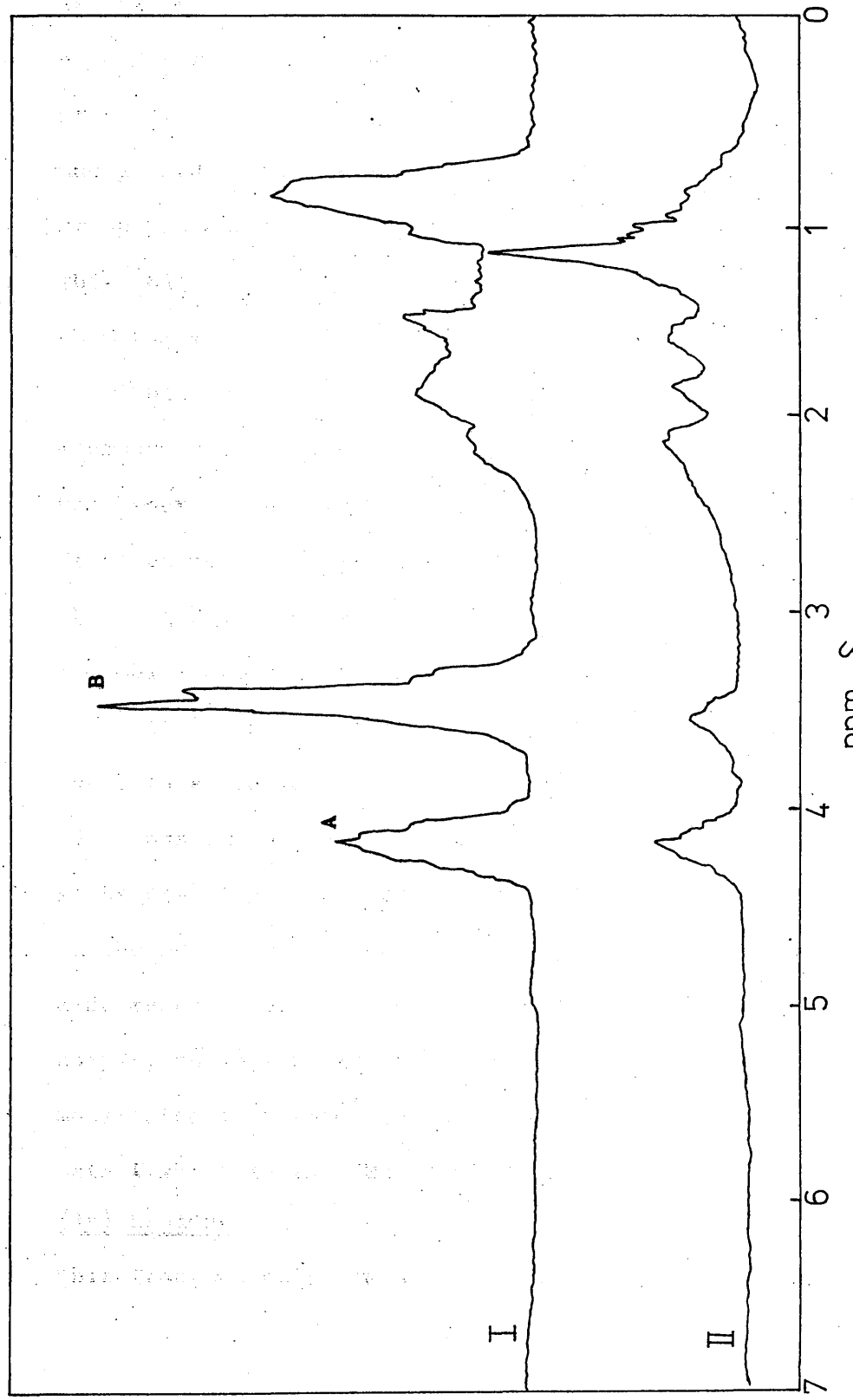


FIGURE 5.13 NMR SPECTRA FOR (I) UNDEGRADED COPOLYMER A2, (II) COLD RING FRACTION FROM COPOLYMER A2.

of these two peaks, which occur at exactly the same δ values as in the original sample. The intensity of each peak is directly proportional to the number of protons contributing to the absorption. This inversion, therefore, suggests a loss of $-C\underline{H}_2Br$ or $O-C\underline{H}_3$ protons with respect to the $-O-C\underline{H}_2-$ protons. The remainder of the spectrum is similar to the undegraded sample with the exception of a shift of the methyl group protons of the methacrylate group to a higher frequency. This shift may originate from deshielding effects or stereochemical modifications arising in the 'cold ring' fraction.

The bromine content of this fraction was obtained by microanalysis and compared with that of the original sample. Copolymer A3 containing 26.5% of bromine, yielded a 'cold ring' fraction which contained 11.7% bromine. Hence, under 45% of the original bromine is retained in the 'cold ring' fraction for this copolymer A3 system.

All of this evidence suggests that the 'cold ring' fraction consists essentially of modified chain fragments. These modifications include a degree of unsaturation due to conjugated sequences of carbon-carbon double bonds, and a general reduction in the number of carbon-bromine bonds. This fraction also shows a decrease in bromine content relative to the original copolymer sample, as well as modifications to the skeletal structure manifested in carbonyl broadening in the infra-red spectrum and methyl shift in the NMR spectrum.

(iv) Residue

This fraction only accounted for about 2% of the original

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(iv) Residue

This fraction only accounted for about 2% of the original

weight of the sample and was consequently not investigated in any detail.

From the thermal analysis techniques discussed earlier, it is obvious that the degradation reaction can be separated into two distinct stages, the relative importance of each stage being a function of the composition of the copolymer. It is clearly important therefore, to characterise the features and products of degradation from each stage. For this purpose a series of isothermal degradations were carried out at selected temperatures for specific time periods and the products of each stage characterised by the methods outlined previously.

5.4 FEATURES OF THE FIRST STAGE OF DEGRADATION

Degradations were carried out for time periods of between one and twenty-four hours at various temperatures in the range 250-330^{o}C. Copolymers A2 and A3 were used almost exclusively in these studies as their compositions were in the intermediate range.

Molecular weight studies could not be carried out at lower temperatures due to the complete insolubility of the polymer in any of the common solvents, after minimal degradation. This gel formation suggested that crosslinked structures were being formed during the very early stages of degradation.

The condensable products from these isothermal degradations were subjected to sub-ambient distillation before subsequent analysis. A typical sub-ambient TVA trace from such an experiment is shown in Figure 5.14. This trace was produced after isothermal degradation of 40mgs of copolymer A2 (69% 2BEM) at

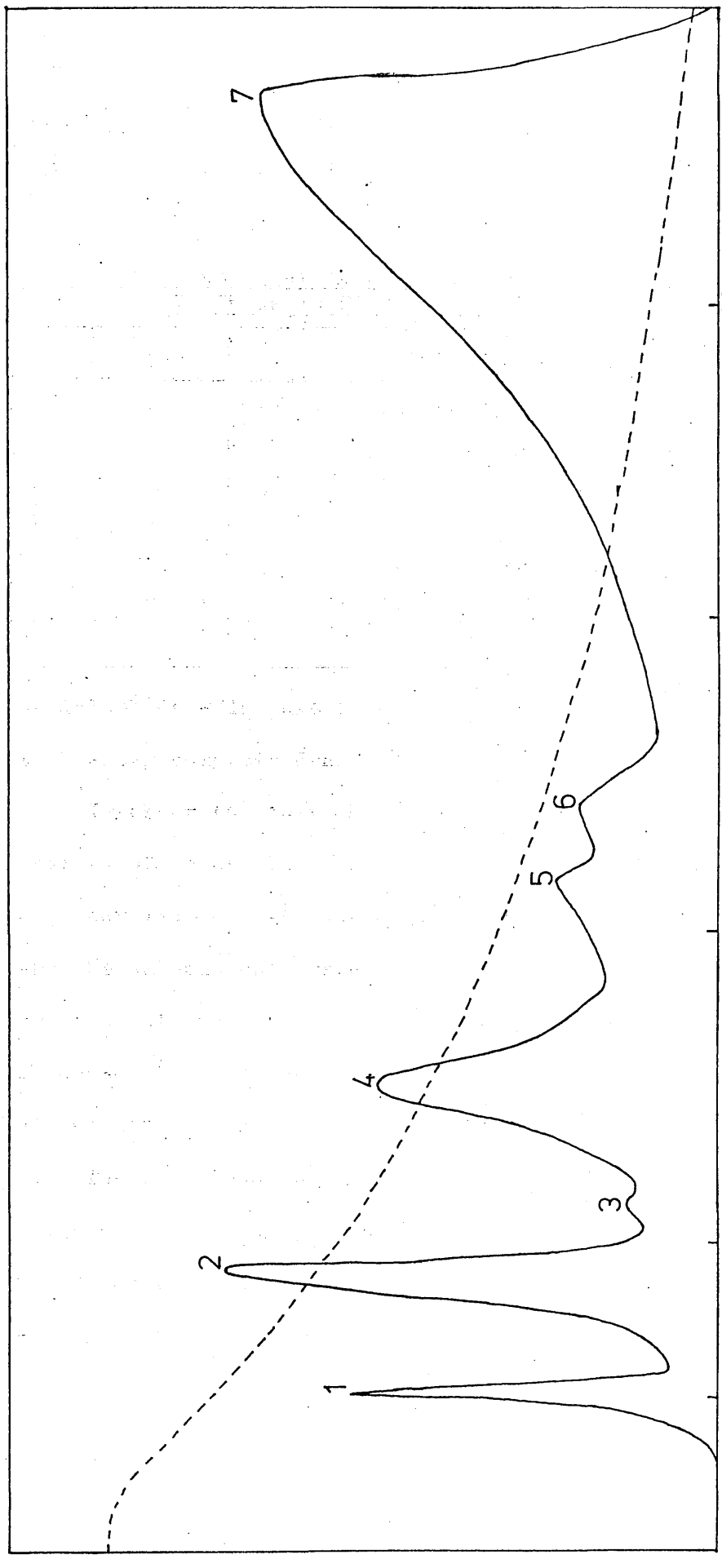


FIGURE 5.14 SUB-AMBIENT TVA TRACE OF PRODUCTS FROM ISOTHERMAL DEGRADATION OF 40 mg COPOLYMER A2 (69% 2BEM) AT 325°C FOR 1 HOUR.

325°C for one hour.

The condensables giving rise to the individual peaks are presented in Table 5.4. These products are qualitatively the same as those identified in the total degradation to 500°C. There are, however, some products such as carbon dioxide and

Table 5.4 Identification of Products from Sub-ambient TVA Shown in Figure 5.14

Peak	Products Identified
1	Carbon Dioxide
2	Methyl Bromide
3	Acetaldehyde
4	Methyl Acrylate
5	Methyl Methacrylate
6	1,2 Dibromoethane
7	2 Bromoethyl Methacrylate

acetaldehyde which are formed in relatively smaller quantities than after complete degradation.

In order to study the products evolved at very low degrees of volatilisation, a series of isothermal degradations were carried out over one hourly periods at 255°C, 260°C and 265°C and the sub-ambient traces illustrated in Figure 5.15 shows the build up of these initial volatiles at lower temperatures. The condensable products were identified as methyl bromide, 1,2 dibromoethane and the two monomers MA and 2BEM.

The actual positions of the peaks in the sub-ambient trace shift to longer retention times with increasing amounts of product, a phenomena common to most chromatographic techniques. A number of interesting conclusions could be drawn from these

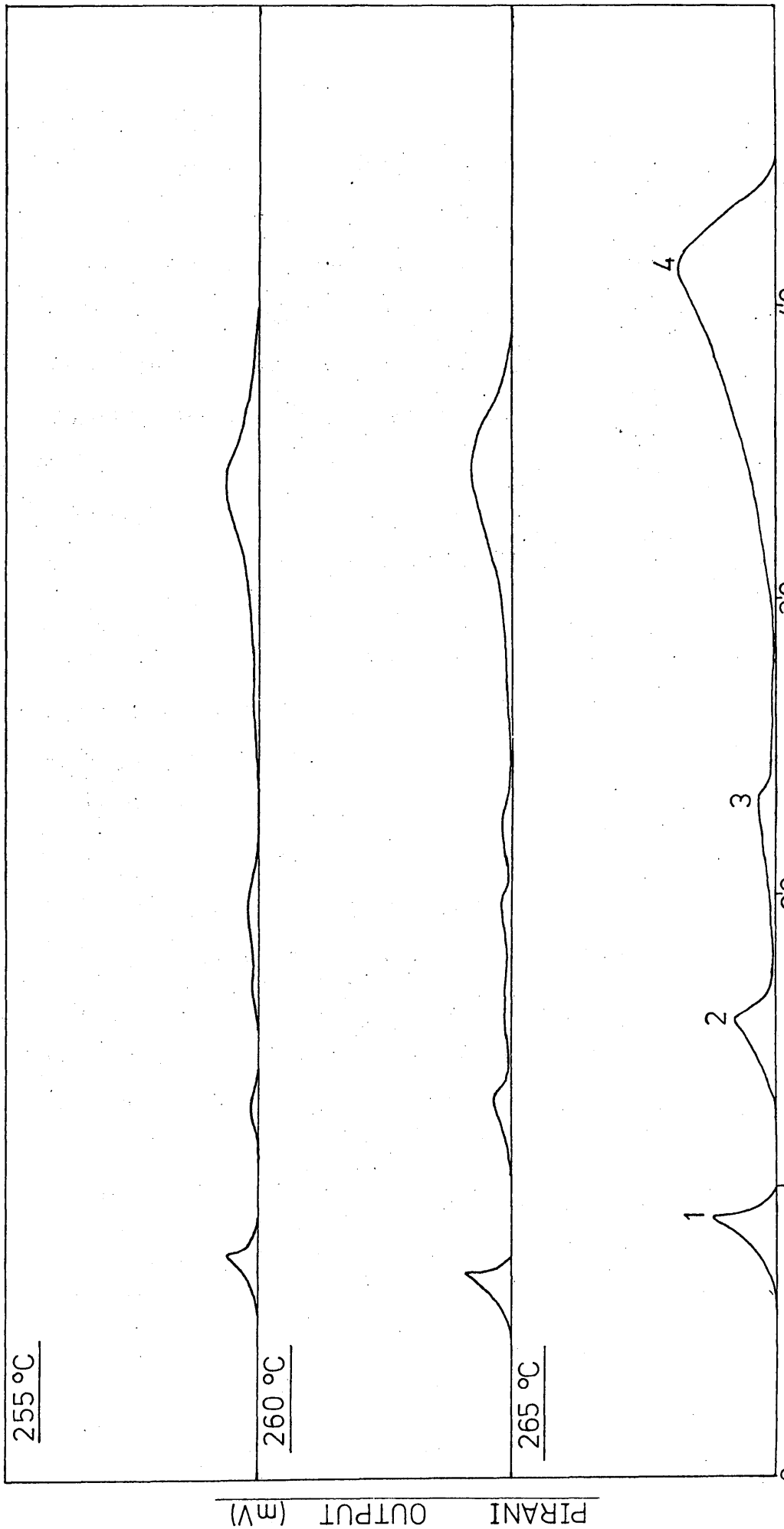


FIGURE 5.15 SUB AMBIENT TVA TRACES FROM ISOTHERMAL DEGRADATION OF 44 mg Copol A2 AT VARIOUS TEMPERATURES FOR 1 HOUR

1 - CH_2Br 2 - MA 3 - 1,2DBE 4 - 2BEM.

results:-

(i) Carbon dioxide production is not associated with methyl bromide formation.

(ii) The appearance of the two monomers at this stage of degradation suggests the existence of a depolymerisation process as one of the initial reactions of degradation.

(iii) The concurrent production of methyl bromide and 1,2 dibromoethane infers that these products may arise from competing reactions of a common precursor, namely the bromomethyl radical ($\bullet CH_2Br$) which can either abstract a proton to form methyl bromide or undergo a combination reaction with a similar radical to form 1, 2 dibromoethane. The relative importance of these two reactions would depend on the availability of a tertiary hydrogen atom for abstraction which in turn is dependent on the copolymer composition. The ratio of the amounts of these two products should therefore, be influenced by the composition of the copolymer if they are competing reactions of the same radical.

As the degradation temperature is increased the production of these four volatiles increases with the additional formation of carbon dioxide, vinyl bromide, acetaldehyde and methyl methacrylate. There are also minor amounts of ethyl methacrylate and bromoethanol, detected by mass spectrometry, produced in this first stage.

The non-condensable products formed at this stage were identified as being mostly methane with small amounts of carbon monoxide and hydrogen.

Most of the 'cold ring' fraction is formed during this initial degradation stage. After isothermal degradation of copolymer A3 at 352°C for one hour the infra-red spectrum of the substantial 'cold ring' fraction was found to be identical to the spectrum obtained from this fraction after complete degradation to 500°C, including the presence of a sharp peak at 1630cm^{-1} due to the unsaturated structures. This shows therefore, that the formation of chain fragments occurs concurrently with the production of the major volatiles and suggests that this fraction may be formed by a competing chain scission step in the overall degradation reaction.

Spectral changes in the heated polymer were monitored by degrading a thin film of polymer cast on a salt plate. This film was heated to selected temperatures and the spectrum obtained was compared with that of the original undegraded sample. Figure 5.16 illustrates selected sections of the spectra of the undegraded sample and the residue of copolymer A2 after the first stage of degradation had been completed (370°C). The most obvious difference in the spectra is the development of a peak at 1630cm^{-1} in the heated sample. This indicates the formation of unsaturation in the residual polymer, similar to that found in the 'cold ring' fraction. The carbonyl region shows slight broadening in the residue spectrum to both higher and lower frequencies. The residue also shows evidence of structural changes with modifications of the fingerprint region below 1100cm^{-1}.

It seems therefore, that the first stage of degradation includes the formation of most of the condensable products

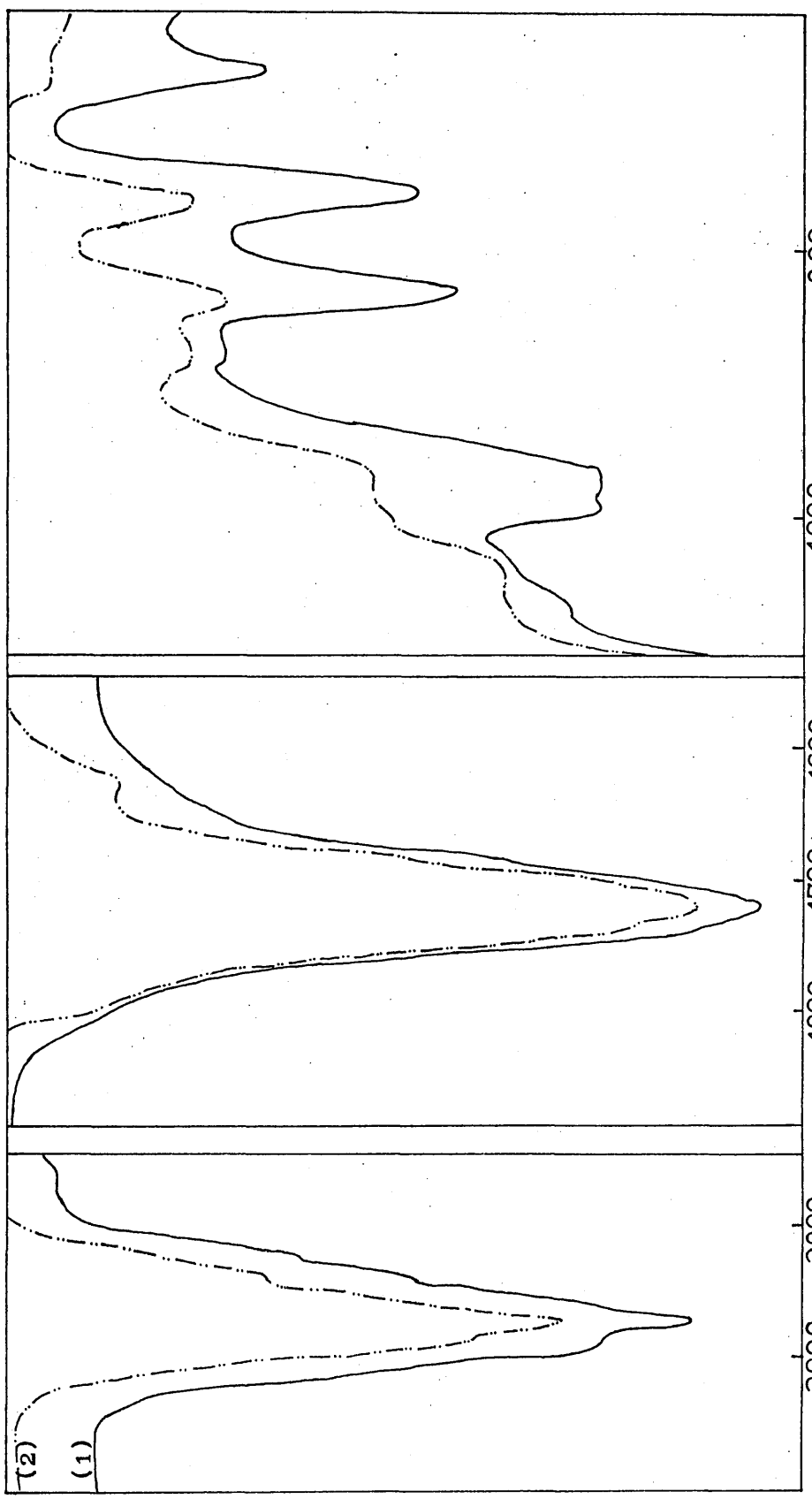


FIGURE 5.16 INFRARED SPECTRUM OF COPOLYMER A2 (1) UNDEGRADED, (2) RESIDUE AFTER DYNAMIC DEGRADATION TO 370°C.

found in the complete degradation process, as well as concurrent production of the chain fragments which make up the 'cold ring' fraction. Non-condensable species, mainly methane are also produced in this stage with the residual coloured polymer showing a degree of unsaturation in addition to undefined structural modifications.

5.5 FEATURES OF THE SECOND STAGE OF DEGRADATION

This secondary stage of degradation accounts for about 10% of the original weight for copolymer A2 and 30% for copolymer A3 which contains a greater proportion of methyl acrylate units. The products from this stage were investigated by degrading the residues from the isothermal degradations discussed in the preceding section.

A typical sub-ambient TVA trace of the condensable products evolved from this volatilisation stage is shown in Figure 5.17. This trace was obtained by thermally degrading the residue of 40mgs of copolymer A3 to 500°C, following isothermal heating at 325°C for two hours. The identification of the peaks is summarised in Table 5.5. The trace indicates that appreciable amounts of carbon dioxide, acetaldehyde and methyl methacrylate are formed in this second stage of decomposition with the additional formation of methanol and chain fragments. The

Peak	Products Identified
1	Carbon Dioxide & traces of Ketene and unsaturated Hydrocarbons
2	Acetaldehyde
3	Methanol
4	Methyl Methacrylate
5	Chain Fragments

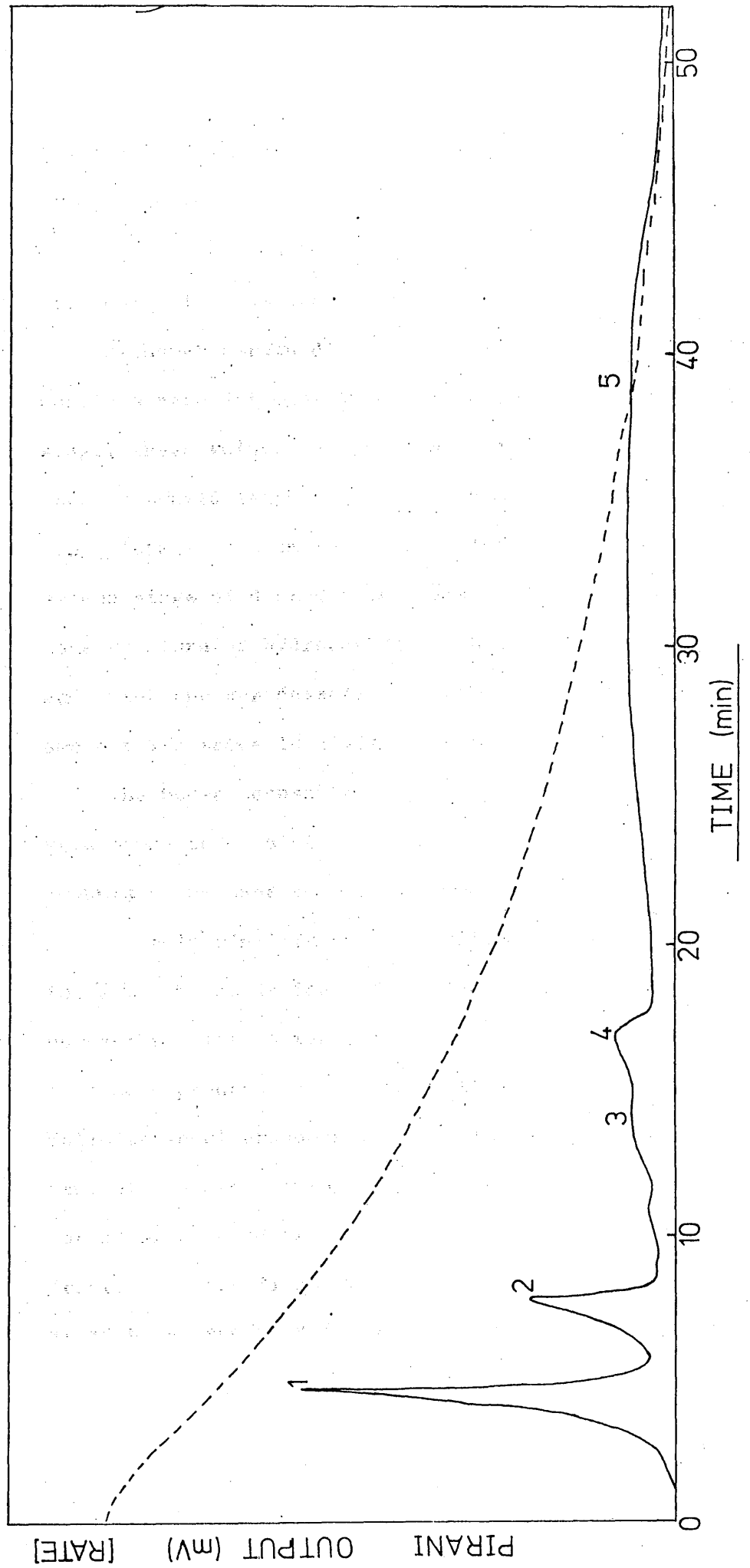


FIGURE 5.17 SUB-AMBIENT TVA TRACE OF PRODUCTS FROM RESIDUE OF COPOLYMER A3 (40 mg) HEATED TO 325°C, HEATED TO 500°C.

molecular weight of these fragments must be less than those which make up the'cold ring' fraction, possibly resembling dimers or trimers of the modified polymer structure. Methyl bromide, 1,2 dibromoethane and the two monomers are absent from the condensable volatiles evolved from this secondary stage of decomposition.

Although carbon dioxide, acetaldehyde and methyl methacrylate were detected amongst the products from the first stage, these volatiles are formed in greater quantities at these elevated temperatures. Both methanol and chain fragments formation seem to be exclusively restricted to this second stage of degradation. Small amounts of ketene and some unsaturated hydrocarbons such as propylene, but-1-ene and but-2-ene were detected in the first peak of the sub-ambient TVA trace in addition to carbon dioxide.

The non-condensable volatiles produced from this stage were found to consist mostly of carbon monoxide with limited amounts of methane and hydrogen.

A 'cold ring' fraction was also formed, although not to the same extent as found from the first stage. It was, however, similar to that first fraction with the exception of a more pronounced broadening of the carbonyl region with a definite shoulder appearing at 1700cm^{-1}. Also, the development of the peak at 1630cm^{-1} due to conjugated sequences was not as pronounced as in the spectrum of the 'cold ring' fraction of the first stage. Very little residue remained after this secondary degradation stage had taken place.

It seems, from the evidence presented, that the second stage of decomposition produces volatiles such as carbon dioxide, methanol and chain fragment which are characteristic of the degradation products of PMA homopolymer. This suggests that the reactions producing the volatiles may be similar to those which occur during PMA decomposition. It was clear from qualitative analysis that methanol production increased from copolymer A2 containing 31% MA units to copolymer A3 containing 52% of MA units indicating that methanol formation may be a function of the number of methyl acrylate units in the copolymer. Acetaldehyde, which is formed to a substantial extent in the second stage is not, however, found among the degradation products of PMA, and may be associated with 2BEM units or with structures formed in the first part of degradation. Carbon monoxide is the chief non-condensable product formed in this stage which suggests the decomposition of ester or ketonic structures in the residual polymer at these higher temperatures. The 'cold ring' fraction shows the development of a carbonyl absorption at 1700cm^{-1} with no obvious peak due to unsaturation.

5.6 QUANTITATIVE STUDY OF THE DEGRADATION PRODUCTS FROM 2BEM-MA COPOLYMERS

Quantitative analysis of methyl bromide and carbon dioxide was carried out using the infra-red spectroscopy technique described in Chapter 2. The calibration plots for both these gases are shown in Figure 2.7. The sub-ambient TVA technique was employed to separate these two products efficiently before subsequent infra-red analysis. The number of moles of each product could be obtained by applying the 'ideal' gas equation,

$PV = nRT$, as described earlier, and ultimately each product was expressed as a percentage weight of the original polymer sample.

Gas-liquid chromatography was employed for quantitative estimation of the following liquid products; methyl acrylate, 2-bromoethyl methacrylate, acetaldehyde, 1,2 dibromoethane, methyl methacrylate, bromoethanol, ethyl methacrylate and methanol. A Perkin Elmer F11 Gas chromatograph with a thermal conductivity detector was employed under the specific conditions outlined in Chapter 2. The sensitivity factors (K) for each of the products relative to the external reference n-hexyl acrylate were found by the integral method outlined in Chapter 2. The calibration plots for these products, with the exception of 2BEM, are shown in Figures 5.18, 5.19 and 5.20. The plot for 2BEM is shown in Figure 2.8, and the sensitivity factors (K) for each product are presented in Table 2.4. The liquid products obtained from degradations of 50mg powdered samples heated to $500^{o}C$ at $10^{o}C$/min under vacuum were analysed under the controlled conditions previously described. For methyl bromide and carbon dioxide estimations, 25 mg samples were degraded under the same conditions as above. Quantitative methyl bromide analysis was also carried out after isothermal degradation of 25mg of powdered sample at $315^{o}C$ for 100 minutes, and compared to those values obtained from total degradation to $500^{o}C$.

A typical chromatogram of the degradation products is shown in Figure 5.21. This trace illustrates the separation of products obtained from copolymer A3 containing 48% 2BEM units.

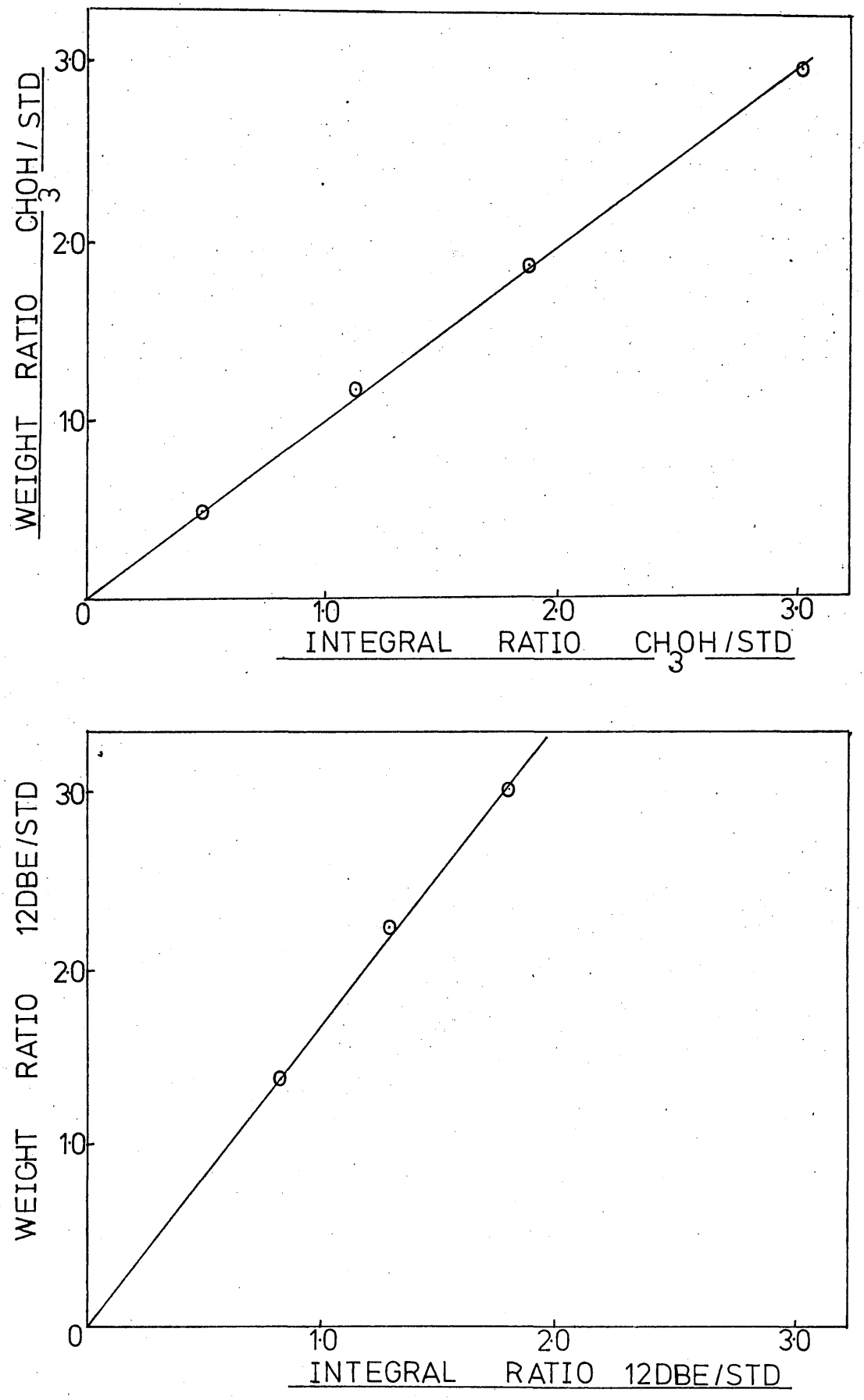
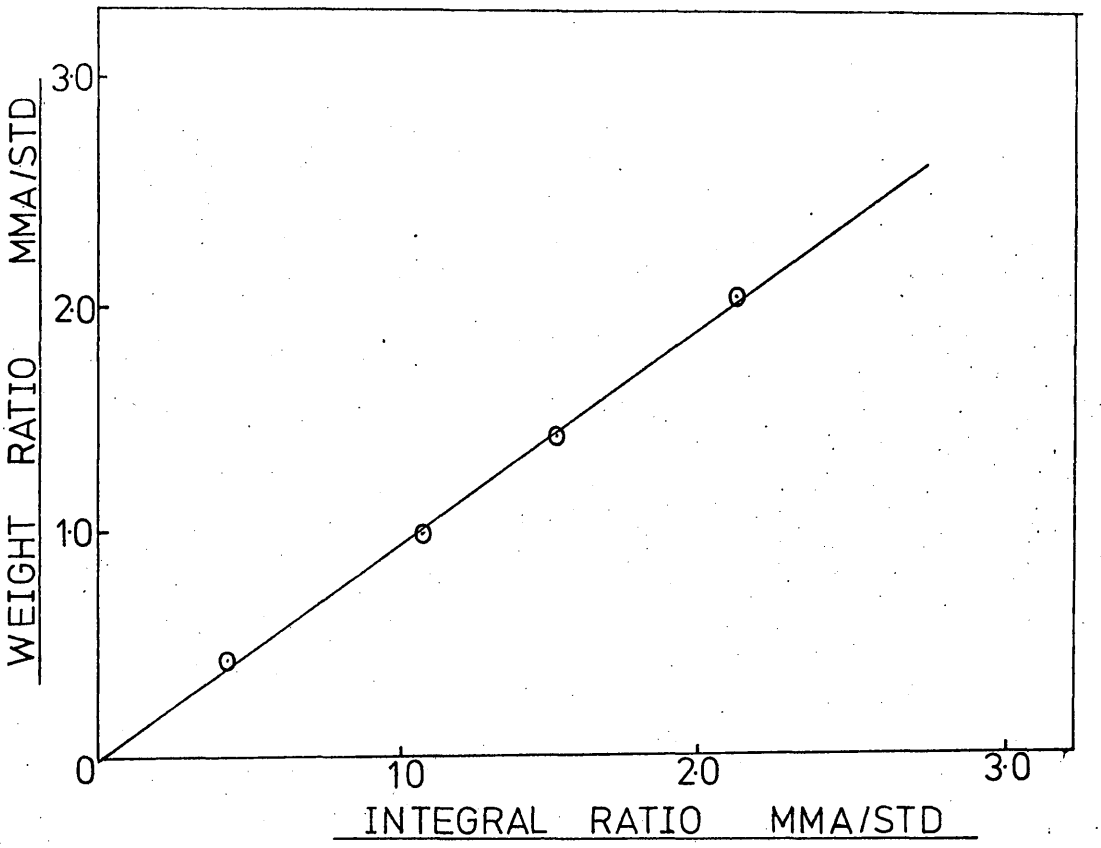


FIGURE 5.18 GLC CABLIBRATION PLOTS FOR METHANOL AND 1,2 DIBROMOETHANE.



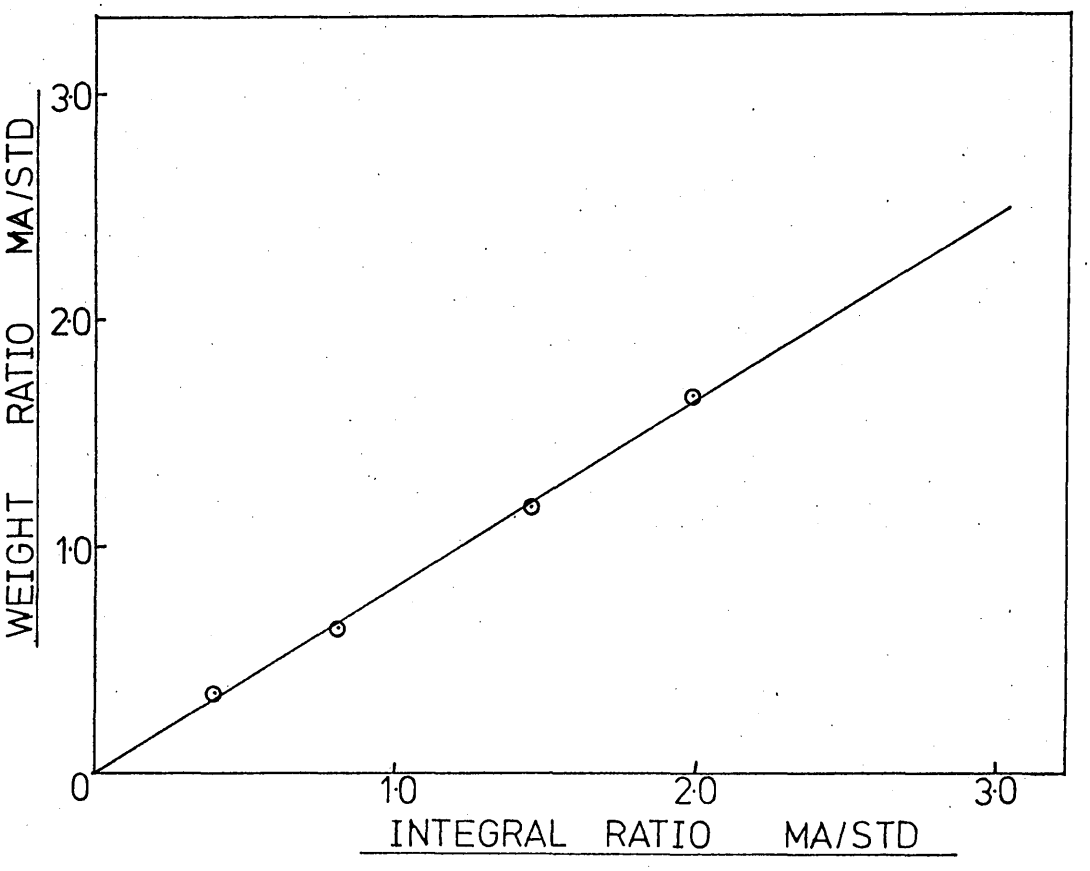
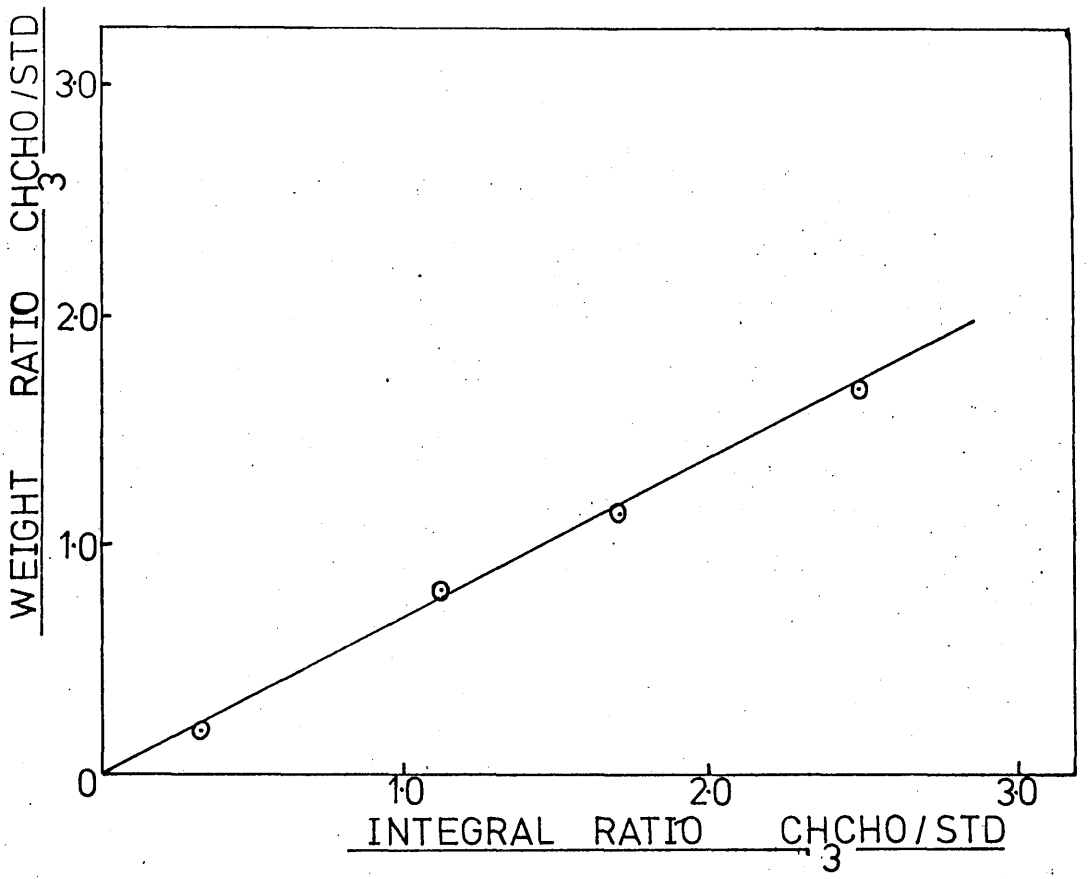


FIGURE 5.19 GLC CALIBRATION PLOTS FOR MMA AND MA.



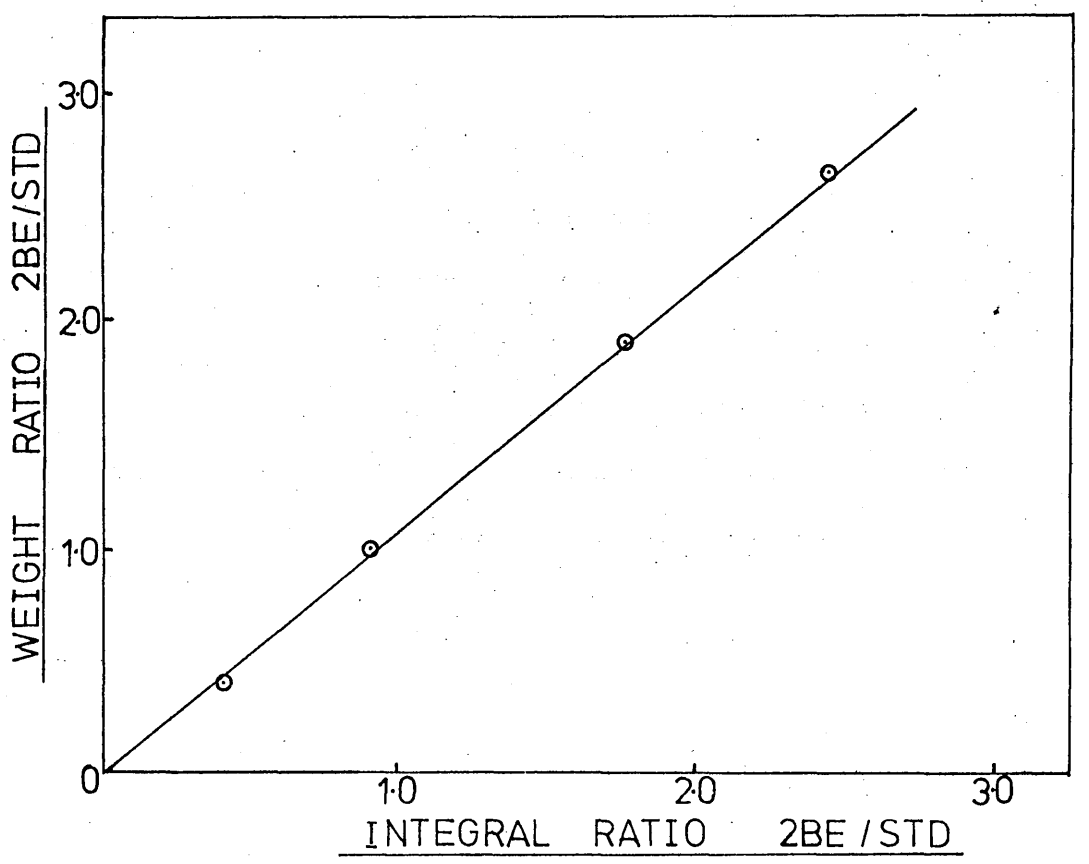


FIGURE 5.20 GLC CALIBRATION PLOTS FOR ACETALDEHYDE AND BROMOETHANOL.

The compound responsible for each peak was identified by comparing the retention times of known standard compounds under these specific condtions. The products giving rise to each peak numbered in the chromatogram are listed in Table 5.6. Apart from ether, which was used as a cleaning agent, all the products were previously identified by the spectroscopic techniques discussed earlier.

The quantitative information on the major degradation products obtained by the techniques outlined above for the four copolymers studied is presented in Table 5.7. The results for P2BEM together with Madorsky's findings for PMA homopolymer are also given.

The first section of the table deals with the copolymer composition which may be expressed as a number and a weight percentage of each monomer. This latter information shows the weight bias of the heavier brominated monomer. It is also useful for comparison with the weight of each product thought to be derived from specific monomer units.

The next section presents the weight of each fraction of degradation to 500^{o}C as a percentage of the original sample weight. The volatile fraction includes the weight loss due to volatilisation of both condensable and non-condensable products from TVA experiments. The average values for all of these fractions were obtained by a series of weight measurements of the degradation tube before and after degradation to 500^{o}C.

The remainder of the Table summarises the quantitative

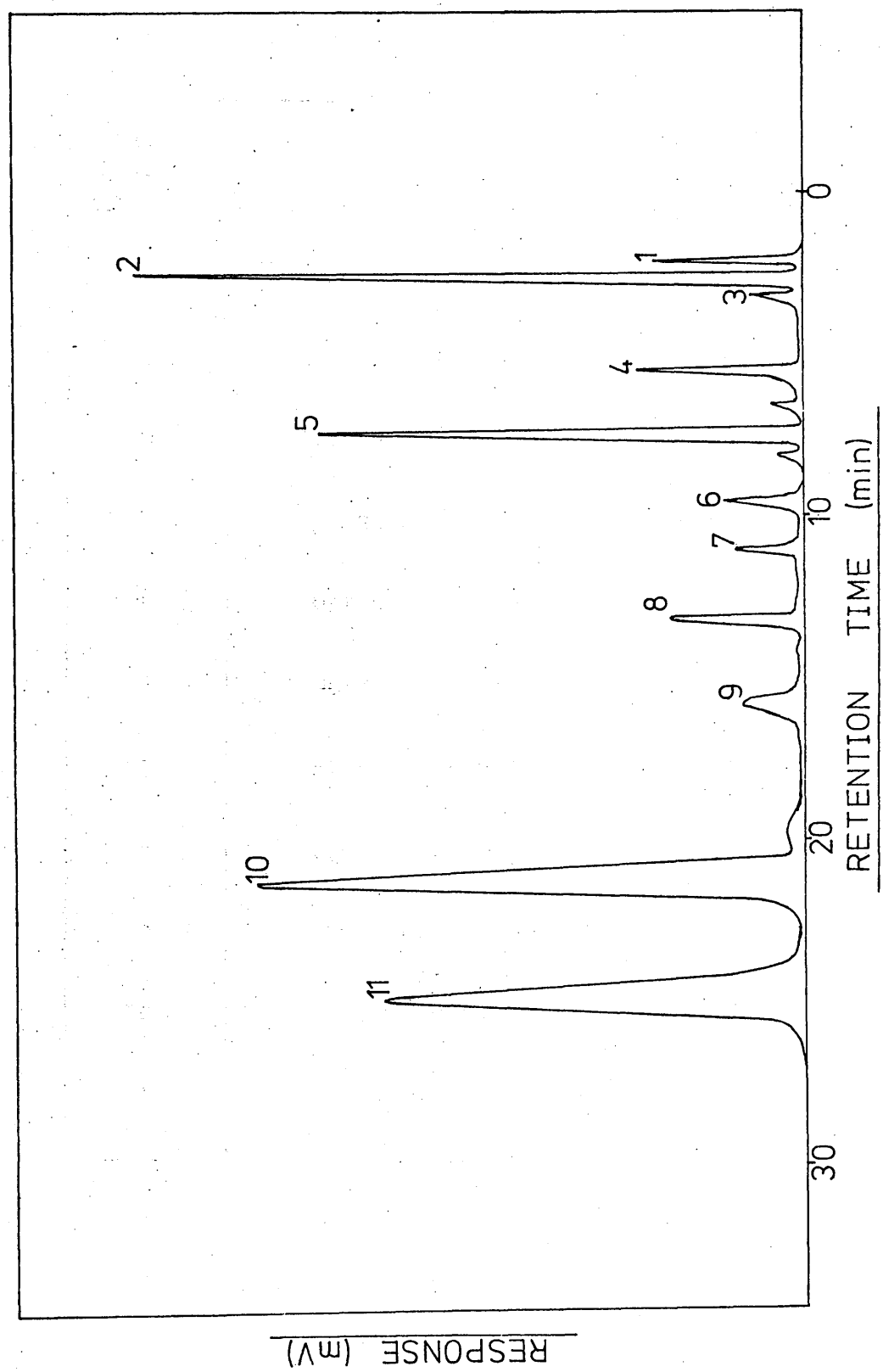


FIGURE 5.21 CHROMATOGRAM OF DEGRADATION PRODUCTS FROM COPOLYMER A3 (50 mgs) HEATED TO 500°C AT 10°C/min.
CARRIER GAS - HELIUM FLOWING AT A RATE OF 40 ml/min; OVEN-AMBIENT TO 150°C AT 10°C/min.

TABLE 5.6

IDENTIFICATION OF PEAKS IN CHROMATOGRAPH ILLUSTRATED IN FIGURE 5.21

PEAK NUMBER	LIQUID PRODUCT
1	METHYL BROMIDE
2	ACETALDEHYDE
3	ETHER
4	METHANOL
5	METHYL ACRYLATE
6	METHYL METHACRYLATE
7	ETHYL METHACRYLATE
8	1,2 DIBROMOETHANE
9	BROMOETHANOL
10	n-HEXYL ACRYLATE (reference)
11	2 BROMOETHYL METHACRYLATE

TABLE 5.7

QUANTITATIVE ANALYSIS OF DEGRADATION PRODUCTS FROM COPOLYMERS OF 2BEM-MA AND RESPECTIVE HOMOPOLYMERS

	P2BEM	A1	A2	A3	A4	PMA*
% MA UNITS	-	19	31	52	91	100
% 2BEM UNITS	100	81	69	48	9	-
WEIGHT % MA UNITS	-	9.7	16.4	34.5	65.0	100
WEIGHT % 2BEM	100	90.3	83.6	65.5	35.0	-
% WT VOLATILES	>98	80	70	65	45	27
% WT OF CRF	-	16	26	31	51	72
% WT OF RESIDUE	-	4	4	4	4	1
2BEM % OF ORIGINAL WT	>98	59	18	12	0.4	-
% Br CONTENT OF TOTAL Br PRESENT	>98	65	21	18	2.2	-
CH_3Br % OF ORIGINAL WT	-	2.7	9.6	12.5	4.2	-
% Br CONTENT	-	6.2	23.3	37.5	24.3	-
1,2 DIBROMOETHANE						
% OF ORIGINAL WT	-	7.2	3.3	1.8	traces	-
% Br CONTENT	-	16.7	8.6	5.6	-	-
METHYL ACRYLATE						
% OF ORIGINAL WT	-	2.9	1.8	2.7	3.6	0.76
% OF MA CONTENT WT	-	30	11.2	8.3	5.7	0.76
METHANOL						
% OF ORIGINAL WT	-	-	0.25	1.0	4	15
% OF MA CONTENT WT	-	-	1.6	3.0	6.2	15
ACETALDEHYDE						
% OF ORIGINAL WT	-	4.0	5.2	9	3.6	-
METHYL METHACRYLATE						
% OF ORIGINAL WT	-	0.2	0.3	0.5	1.12	traces
CARBON DIOXIDE						
% OF ORIGINAL WT	trace	1.7	2.0	3.3	6.1	7.5
% MA CONTENT WT	-	18	11.9	9.6	9.4	7.5
2 BROMOETHANOL						
% OF ORIGINAL WT	-	2.3	1.5	1.0	0.1	-
% Br CONTENT	-	3.8	2.8	1.5	0.4	-
ETHYL METHACRYLATE						
% OF ORIGINAL WT	-	1.2	0.7	0.4	0.1	-

*From S. L. Madorsky 54

production of the major condensable products expressed as a percentage weight of the original polymer sample. For brominated volatiles this information has been used to calculate the bromine content of each brominated compound as a percentage of the original weight of bromine in the undegraded copolymer e.g. 37.5% of the bromine in copolymer A3 is lost during degradation as methyl bromide.

For carbon dioxide, methanol and methyl acrylate, the percentage weight of each product has been related to the weight of the methyl acrylate content in the original copolymer sample, and expressed as a percentage of that weight, e.g. 30% of the weight due to methyl acrylate in copolymer A1 is lost as methyl acrylate monomer.

A detailed discussion of the consequences of the quantitative information presented in Table 5.7 and the conclusions which may be drawn from that information will be given later in Chapter 7.

CHAPTER 6

THERMAL DEGRADATION OF P2BEM/PMA BLENDS

6.1 INTRODUCTION

The homopolymers used in this study were identical to those whose degradation behaviour was discussed earlier in Chapter 4. This chapter describes, in a qualitative way, the various features of the thermal breakdown of 1:1 by weight blends of P2BEM and PMA. Such a study of the interactions of the respective monomer units in the copolymer and blend environments can lead to a better understanding of the processes which prevail during the decomposition of the respective homopolymers, and the type of reactive intermediates which exist during these processes.

The blends were studied in the form of thin films cast under vacuum on to the bottom of the degradation tube by the method outlined in Chapter 2. Only blends of a 1:1 by weight ratio were investigated, each film being pre-heated to 120^{o}C for one hour to remove residual solvent. The thin films thus formed were virtually transparent, indicating

reasonable compatibility with good dispersion of the two polymer phases. The structure of the blend consists of a continuous phase of one polymer and a dispersed phase of the other, so that domains of a single polymer are separated by phase boundaries from the domains of the other polymer. The interactions which may occur in the blend in competition with the homopolymer degradation processes, may be grouped into two categories, comprising reactions taking place in the bulk of one or other or both domains, and reactions occurring at phase boundaries. The compatibility and dispersion properties of both systems will determine the relative importance of each type of reaction in any polyblend system. Bulk interactions may occur when small molecules or radicals evolved from one degrading homopolymer diffuse into the domain of the other polymer and react with a macromolecule, macroradical or another small reactant. Interaction at phase boundaries may take place between two macromolecules or a macroradical and a macromolecule. In the latter case therefore, the degree of dispersion, reflected by the opacity of the polyblend film, will have an important bearing on the observed degradation behaviour.

In the copolymer, both monomers are part of an integrated molecular chain system with neighbouring units able to participate in both intra-and intermolecular reactions. In the polyblend system, however, only the latter type of reaction is possible and may occur at the phase interfaces.

6.2 THERMAL ANALYSIS

The TVA trace obtained from a thin film of 30mgs of the 1:1 blend is illustrated in Figure 6.1. It is evident from the TVA thermogram that two main stages of volatilisation take place with the two peaks having T_{max} values at 361°C and 401°C. The temperatures at which maximum rates of volatilisation occur between the T_{max} values of P2BEM and PMA homopolymers which occur at 330°C and 416°C respectively.

The low temperature volatilisation profile of the methacrylate homopolymer is again evident in the blend system. These minor volatilisation peaks were attributed to evolution of occluded monomer and chain-end initiated depolymerisation reactions.

The 0°C trace is substantially separated from the -45°C trace from 200°C, through the first peak maxima, to 380°C, which suggests the formation of a high boiling product, probably 2BEM monomer, in this temperature range. Above 380°C, the 0°C and the -45°C traces are co-incident indicating the cessation of formation of this monomer above this temperature. This is in agreement with the information from P2BEM homopolymer which depolymerises completely by 390°C. The closely grouped -45°C, -75°C and -100°C traces leave the baseline around 300°C, exhibit a shoulder at 325°C and rise to meet the 0°C trace at the second peak maxima. These traces then form a low plateau at higher temperatures. The initial response from these traces occurs some 40°C lower than in PMA, P2BEM showing virtually no response from these traces at any stage of the degradation.

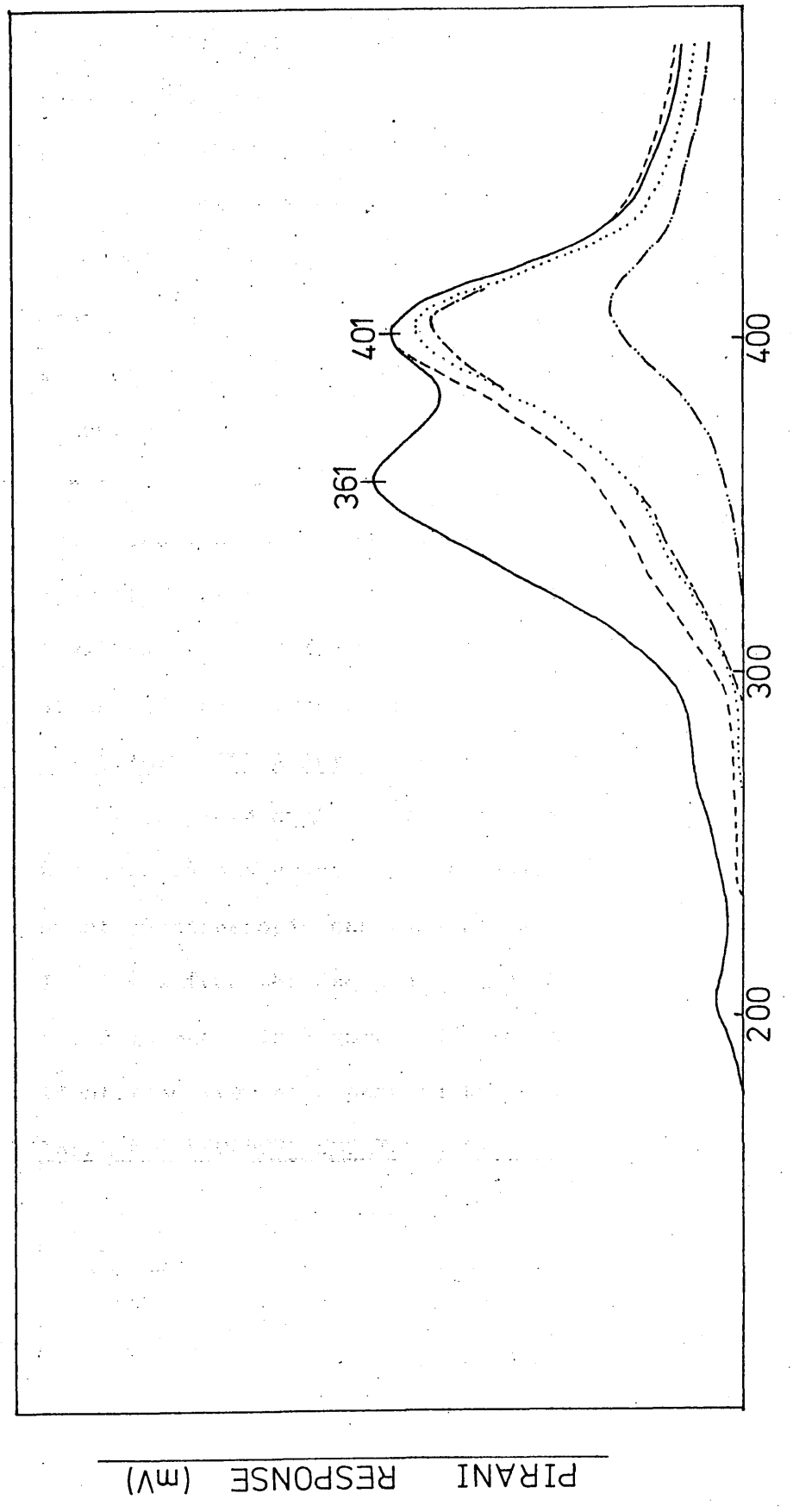


FIGURE 6.1 TVA TRACE OF 1:1 BLEND BY WEIGHT OF P2BEM/PMA (60 mg) SOLVENT-ACETONE PREHEATED TO 120°C FOR 1 HOUR.

This anomalous shoulder at 325°C therefore, may represent an interaction of the two degrading homopolymers which gives rise to volatiles condensed by these various traps. This interaction occurs in a similar temperature range to the first volatilisation peak observed in the copolymer system.

The -196°C trace shows an initial response at 325°C, 40°C lower than PMA, and reaches a maximum rate at a temperature co-incident with the T'max of the second peak. This trace does not leave the baseline in P2BEM homopolymer. The concurrent production of non-condensable species with the condensable products of the anomalous shoulder suggests that both fractions may be evolved from competing steps of the same overall reaction.

A yellow coloured 'cold ring' fraction is observed at the end of the TVA experiment, with little residue remaining at 500°C.

6.3 QUALITATIVE ANALYSIS OF THE DEGRADATION PRODUCTS

A complete qualitative analysis of the condensable products was carried out using the sub-ambient TVA technique with subsequent spectroscopic analysis of each fraction. The sub-ambient TVA trace from the degradation to 500°C of 30mgs of the 1:1 blend is shown in Figure 6.2. Table 6.1 summarises the products identified from each peak in the trace.

TABLE 6.1 PRODUCTS CORRESPONDING TO PEAKS IN FIGURE 6.2

Peak	Products Identified
1	Carbon Dioxide, Ketene (minor)
2	Methyl Bromide, Vinyl Bromide (minor) Acetaldehyde
3	Methanol, Minor products - Methyl Acrylate, 1,2 Dibromoethane, Methyl-methacrylate.
4	Methyl methacrylate, Methyl acrylate, 1,2 Dibromoethane
5	2-Bromoethyl Methacrylate

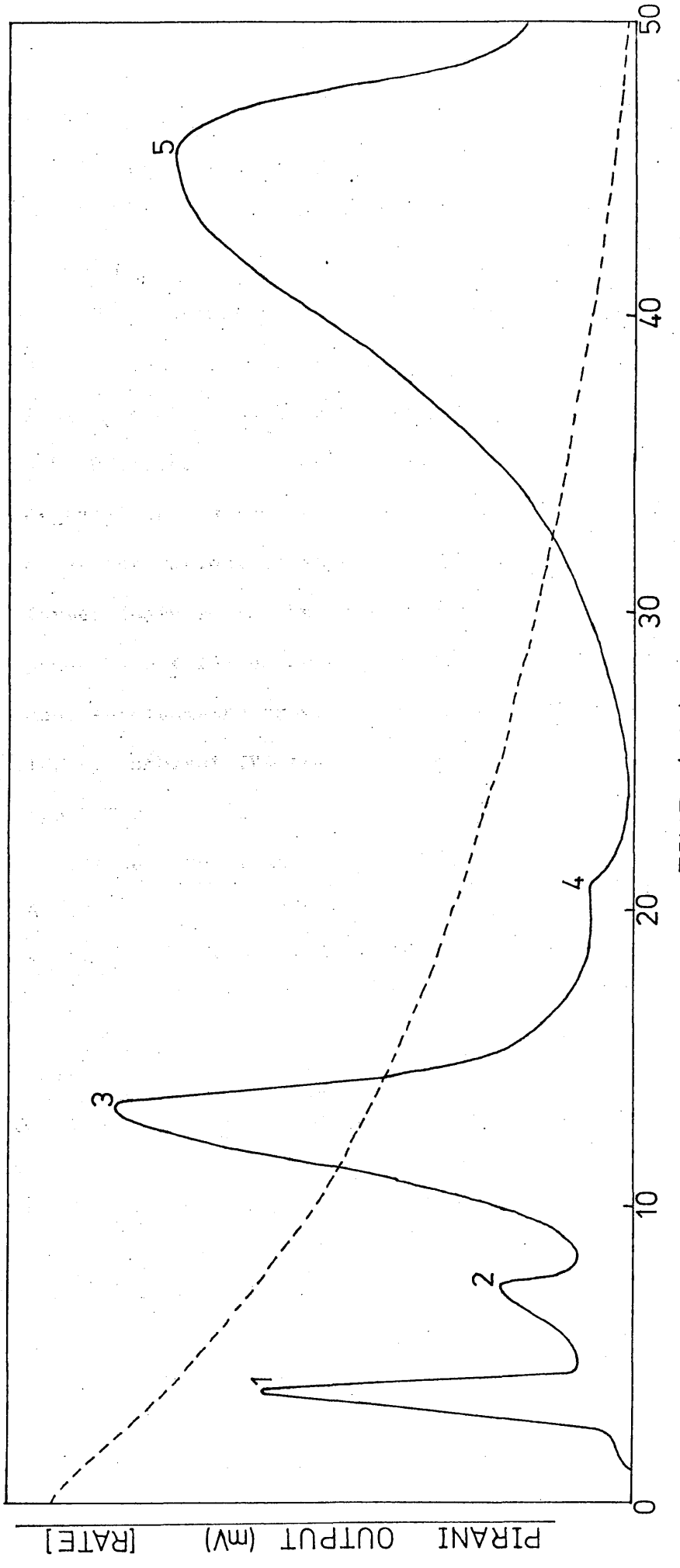


FIGURE 6.2 SUB-AMBIENT TVA TRACE OF DEGRADATION PRODUCTS OF 1:1 BLEND P2BEM/PMA BY WEIGHT DEGRADED TO 500°C AT 10°C/min.

Methyl Bromide, 1,2 Dibromoethane and traces of acetaldehyde and Ketene were observed among the degradation products, in addition to those from the respective homopolymer systems. The amount of MMA produced from this blend system is substantially greater than could be expected from the equivalent amount of PMA present.

The TVA thermogram suggested that the occurrence of the products such as methyl bromide and 1,2 dibromoethane may be linked to the anomalous behaviour shown by the -45°C, -75°C and -100°C traces at temperatures in the region of 325°C. Isothermal degradations therefore, were carried out in this temperature range for various time periods and the condensable products formed analysed in the usual manner. As the amounts of the products not formed by either homopolymer degradation is small, mass spectrometry proved especially useful in these studies. The sub-ambient TVA trace for the isothermal degradation at 310°C for 85 minutes is shown in Figure 6.3. The identification of the numbered fractions in this trace is summarised in Table 6.2.

TABLE 6.2 IDENTIFICATION OF FRACTIONS IN THE SUB-AMBIENT TRACE ILLUSTRATED IN FIGURE 6.3

Peak	Products Identified
1	Carbon Dioxide
2	Methyl Bromide, traces of Vinyl Bromide
3	Methanol, Methyl Acrylate (minor)
4	1,2 Dibromoethane, Methyl Methacrylate
5	2-Bromoethyl Methacrylate

Table 6.2 shows that methyl bromide and 1,2 dibromoethane

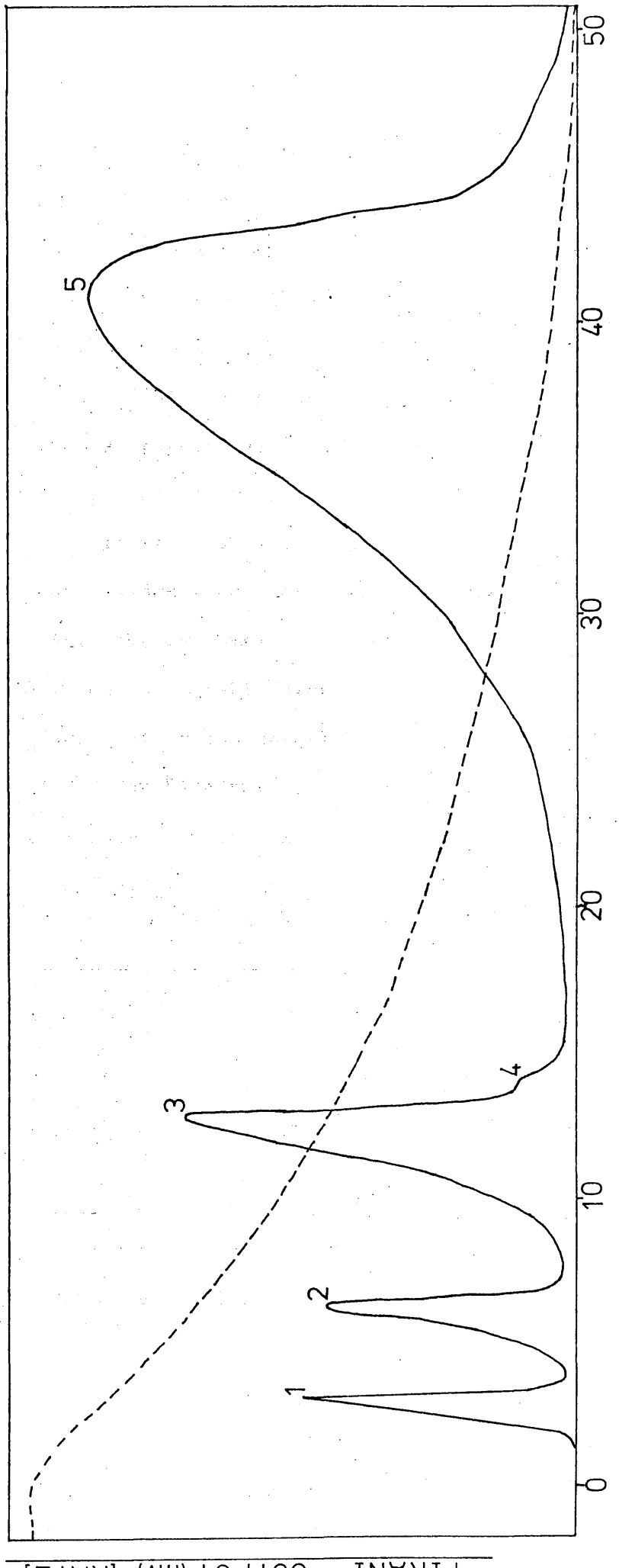


FIGURE 6.3 SUB-AMBIENT TVA OF CONDENSABLE PRODUCTS FROM ISOTHERMAL DEGRADATION AT 310°C FOR 85 min. 30 mg OF 1:1 BLEND P2BEM/PMA.

are produced concurrently from this first stage of degradation, which supports the proposal made earlier in the discussion of the copolymer degradations, that both these products are formed in competing reactions of the common bromomethyl ($\cdot CH_2Br$) free radical precursor. It is clear from these qualitative studies that methyl bromide is produced in greater quantities than 1,2 dibromoethane. The rest of the products may be accounted for in terms of the homopolymer decompositions, although the amount of MMA produced is slightly higher than could be expected from the amount of PMA present in the blend.

The second stage of the degradation was studied by heating the residue from these isothermal degradations to 500°C at 10°C/min. The sub-ambient TVA trace, illustrated in Figure 6.4, is of the condensable products evolved from degradation of the residue formed after isothermal heating of 30mgs of the 1:1 blend at 310°C for 85 minutes. The numbered peaks were identified by mass spectrometric analysis and are presented in Table 6.3.

TABLE 6.3 IDENTIFICATION OF FRACTIONS IN THE SUB-AMBIENT TVA TRACE ILLUSTRATED IN FIGURE 6.4

Peak	Products Identified
1	Carbon Dioxide and Ketene (minor)
2	Acetaldehyde
3	Methanol and Methyl Acrylate (minor)
4	Methyl Methacrylate
5	Chain Fragments

This stage is characterised by the production of condensables which are found from PMA hompolymer decomposition. Acetaldehyde

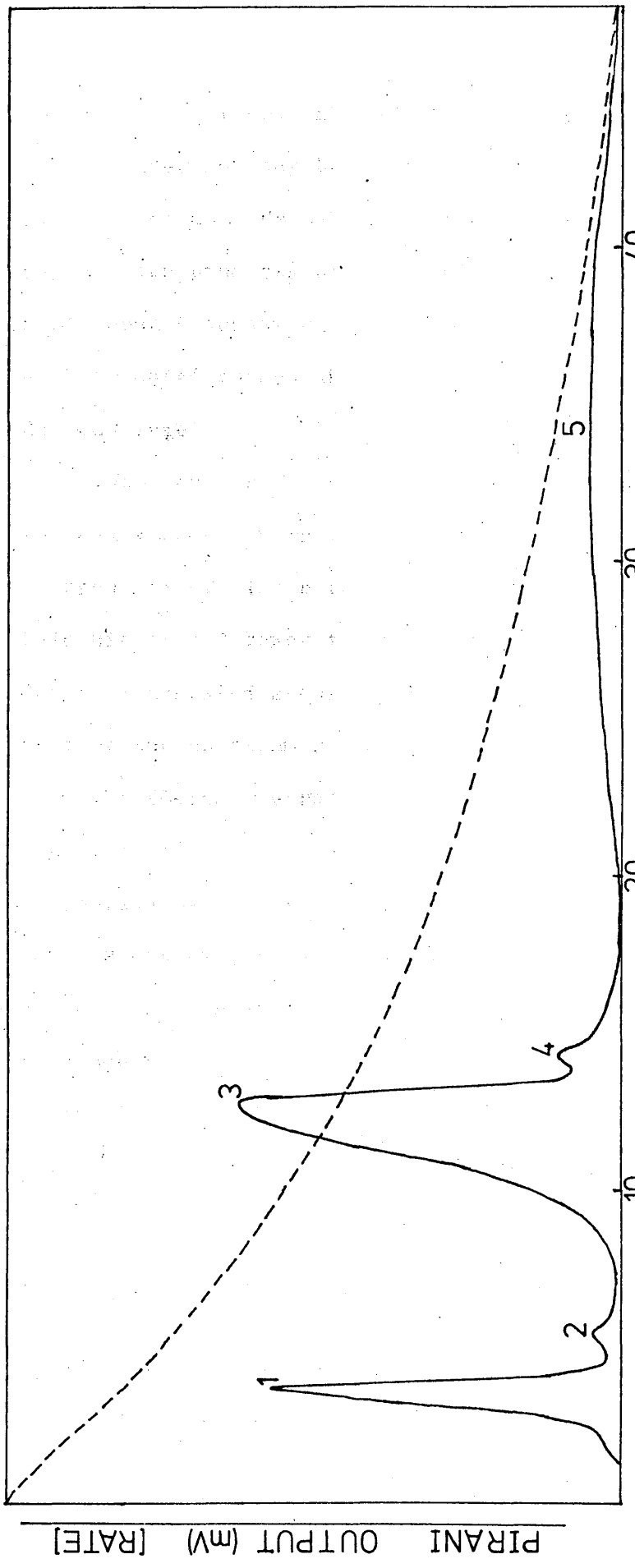


FIGURE 6.4 SUB-AMBIENT TVA TRACE OF CONDENSABLE PRODUCTS FROM DEGRADATION OF RESIDUE OF 30 mg 1:1 BLEND HEATED ISOTHERMALLY AT 310°C FOR 85 min. PROGRAMMED HEATING TO 500°C.

however, is formed in this stage although as a minor product, certainly to a far smaller extent than methyl bromide production in the first stage. Ketene is also produced at these elevated temperatures and may be associated with the acetaldehyde formation reaction. Methyl methacrylate is again present among the degradation products of this stage and is responsible for the small peak 4 appearing as a shoulder on peak 3 in Figure 6.4. No brominated condensables are evolved from this second degradation stage.

The 'cold ring' fraction produced from the TVA experiments was analysed by infra-red spectroscopy as a solution in carbon tetrachloride. The carbonyl region showed slight broadening to both higher and lower frequencies, with a new peak at 1630cm^{-1} due to conjugated sequences of carbon-carbon double bonds. The rest of the spectrum resembled that of PMA homopolymer.

The thermal degradation characteristics of the 1:1 blend system confirmed that an interaction between the degrading homopolymers gave rise to concurrent production of methyl bromide and 1,2 dibromoethane at temperatures in the region of 300 - 360^{o}C. This interaction must occur in an intermolecular fashion to produce bromomethyl free radicals which undergo hydrogen abstraction or combination reactions to form the respective brominated compounds. Proposed mechanisms of formation of this free radical precursor will be discussed in the following chapter. The blend also produces MMA monomer in greater quantities than could be expected from the PMA content present, and may be associated with the bromomethyl radical forming reaction.

Acetaldehyde and ketene are also formed in this polyblend system, although to a much lesser extent than the brominated species, at temperatures in excess of 360°C. The formation of these products may be associated with 2BEM units or with structures formed by the interaction of the two polymer systems.

CHAPTER 7

DISCUSSION OF THE THERMAL DECOMPOSITION OF 2BEM-MA COPOLYMERS AND POLYBLEND WITH PROPOSED REACTION MECHANISMS

7.1 INTRODUCTION

The previous two chapters have dealt with the qualitative and quantitative aspects of the thermal degradation of 2BEM-MA copolymers and a description of the decomposition products from 1:1 blends of the two homopolymers. The following section will attempt to rationalise each feature of the copolymer decomposition by discussing possible mechanistic pathways to the formation of particular degradation compounds leading ultimately to the formulation of an integrated reaction sequence.

The three thermo-analytical techniques, TGA, DSC and TVA show clearly that the low temperature volatilisation reaction which takes place in P2BEM homopolymer, attributed to chain-end initiated depolymerisation, is absent from the degradation profile of each copolymer. The non-appearance of this reaction, even at high methacrylate content, as in copolymer A1, may be

explained in two ways. The first and most obvious explanation is that as in MMA-acrylonitrile copolymers,[69] units of the second monomer block the depropagation reaction. This unzipping process causes a 6% weight loss in P2BEM homopolymer which has an average molecular weight of 333,000. Copolymer A1 therefore, containing 81% 2BEM units, with an average molecular weight of 415,000 should be expected to exhibit some low temperature weight loss. However, this copolymer shows no sign of volatilisation until the first stage of degradation beginning at 300^{o}C. This means that either the MA units have a disproportionally greater effect at these lower temperatures than can be expected by their content which was found to be the case in the MMA-acrylonitrile system[70] or that some other effect is present. The blocking efficiency of the MA group in this system, however, is not complete as MA monomer is found among the degradation products.

The second explanation of the absence of the terminally initiated reaction is that, as in the copolymerisation of MMA-styrene copolymers,[71,72] the presence of the second monomer favours combination rather than disproportionation as the termination step in the polymerisation process. In this way, the proportion of terminally unsaturated structures is drastically reduced even in copolymers containing quite small proportions of styrene. Since the relevant copolymerisation data for this 2BEM-MA system are not available an assessment of this possibility cannot be made.

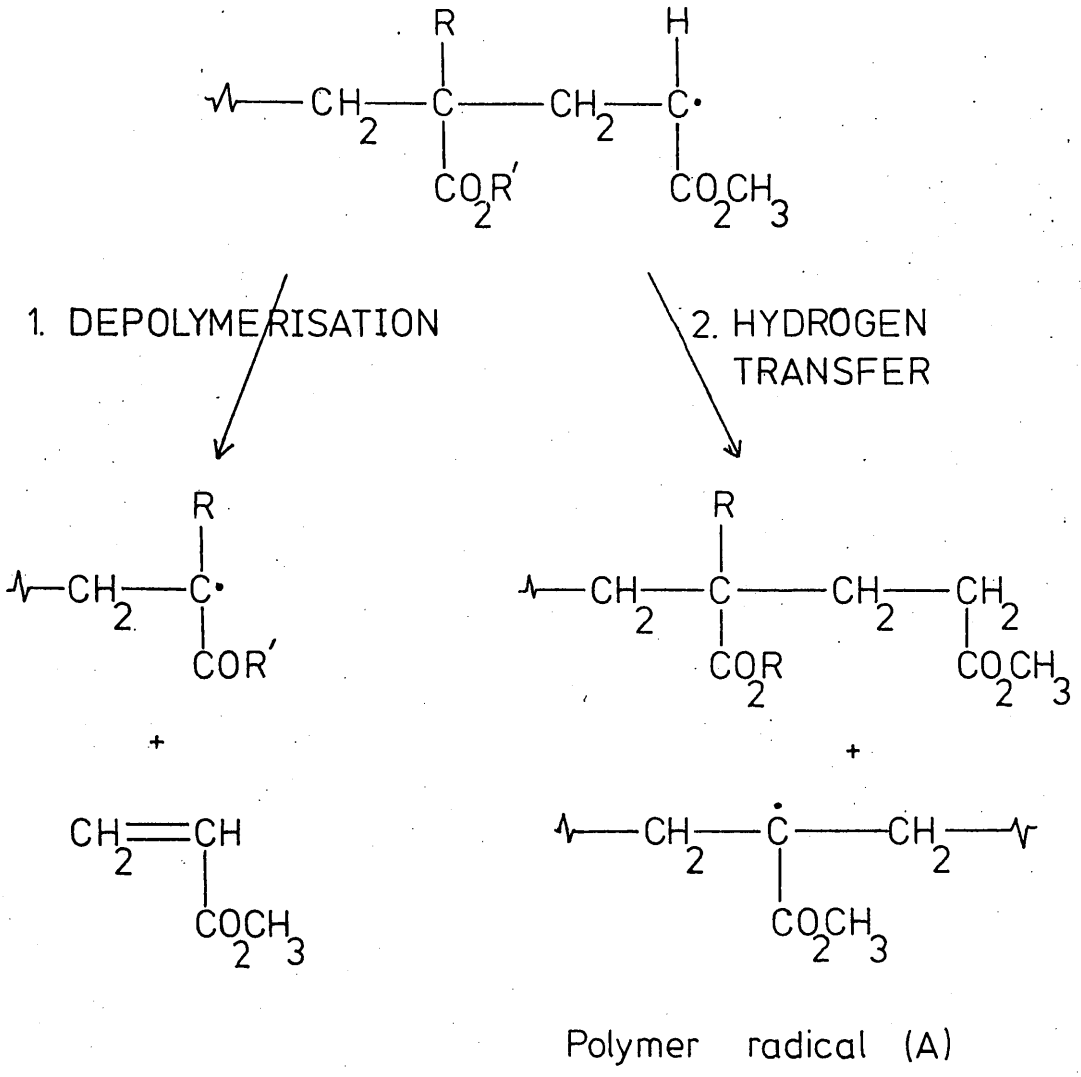
The fact that the copolymer composition has no influence on the initial degradation temperature suggests that the absence

of the low temperature peak in the volatilisation thermograms of each copolymer may be qualitatively accounted for in terms of the decrease in the proportion of unsaturated chain-ends, although some contribution from the blocking reaction of the MA units, especially at low temperatures, cannot be entirely eliminated.

7.2 MONOMER PRODUCTION

It has been shown that both monomers, 2BEM and MA, are formed in the first stage of decomposition of the copolymers, in the temperature range 300-380°C. Figure 5.15 illustrates that the two monomers are among the very first volatiles to be formed during degradation. This suggests that a depolymerisation reaction must occur during the very early stages of decomposition. The production of 2BEM in Table 5.2 clearly shows a progressive inhibition of this unzipping process with increasing MA content. This trend can be accounted for by considering the degradation processes which occur during PMA decomposition, which have been discussed earlier. These transfer reactions yield mainly chain fragments with only minor amounts of monomer. It is therefore, no surprise to find not only a reduction in 2BEM formation with increasing MA content but a concurrent increase in the amount of chain fragments formed, which make up the 'cold ring' fraction of the degradation products. Initiation is thought to take place probably at a methacrylate unit by a random chain scission process, although the possibility of chain-end initiation cannot be ruled out entirely. Once initiation has taken place, unzipping of the 2BEM units occurs until a MA unit is reached.

There are then two possible reactions which this terminal MA radical can undergo, the relative importance of each being dependent on the copolymer composition. The first is that depolymerisation may proceed through this unit to form MA monomer.



Polymer radical (A)

This reaction is most probable when MA units are isolated, i.e. when the MA content is low. Table 5.2 shows that in copolymer A1, 30% of the MA units are liberated as monomer,

with a progressive decrease in this figure as the MA content of the copolymer increases. This figure of roughly one in four MA units being liberated as monomer at low MA content is in accordance with results for the MMA-MA copolymer system studied by Grassie and Torrance.[58] These workers interpreted this ratio as a measure of the relative probabilities of depropagation and transfer occurring at a long chain radical terminated by a MA unit. In copolymers containing higher proportions of MA in which a larger number of MA units will occur in groups depropagation will be inhibited as in PMA, and the above relationship breaks down, as is shown in Table 5.2.

As the copolymer becomes increasingly like PMA, the terminal MA radical may undergo transfer reactions similar to those found in the acrylate homopolymer. The result of these reactions is to form a saturated chain-end and a polymer radical of the type A which is thought to be present in the thermal breakdown of PMA. As in PMA, this reaction may occur intramolecularly or intermolecularly, and will become increasingly important as the MA content of the copolymer increases.

It seems therefore, that once initial random chain scission occurs depolymerisation takes place to produce both monomers and polymer radicals of type A, the concentration of which will increase with increasing MA content.

7.3 METHYL BROMIDE AND 1,2 DIBROMOETHANE FORMATION

As discussed previously, the concurrent production of these two products during the first stage of degradation in both the copolymer and blend systems suggested that each product is

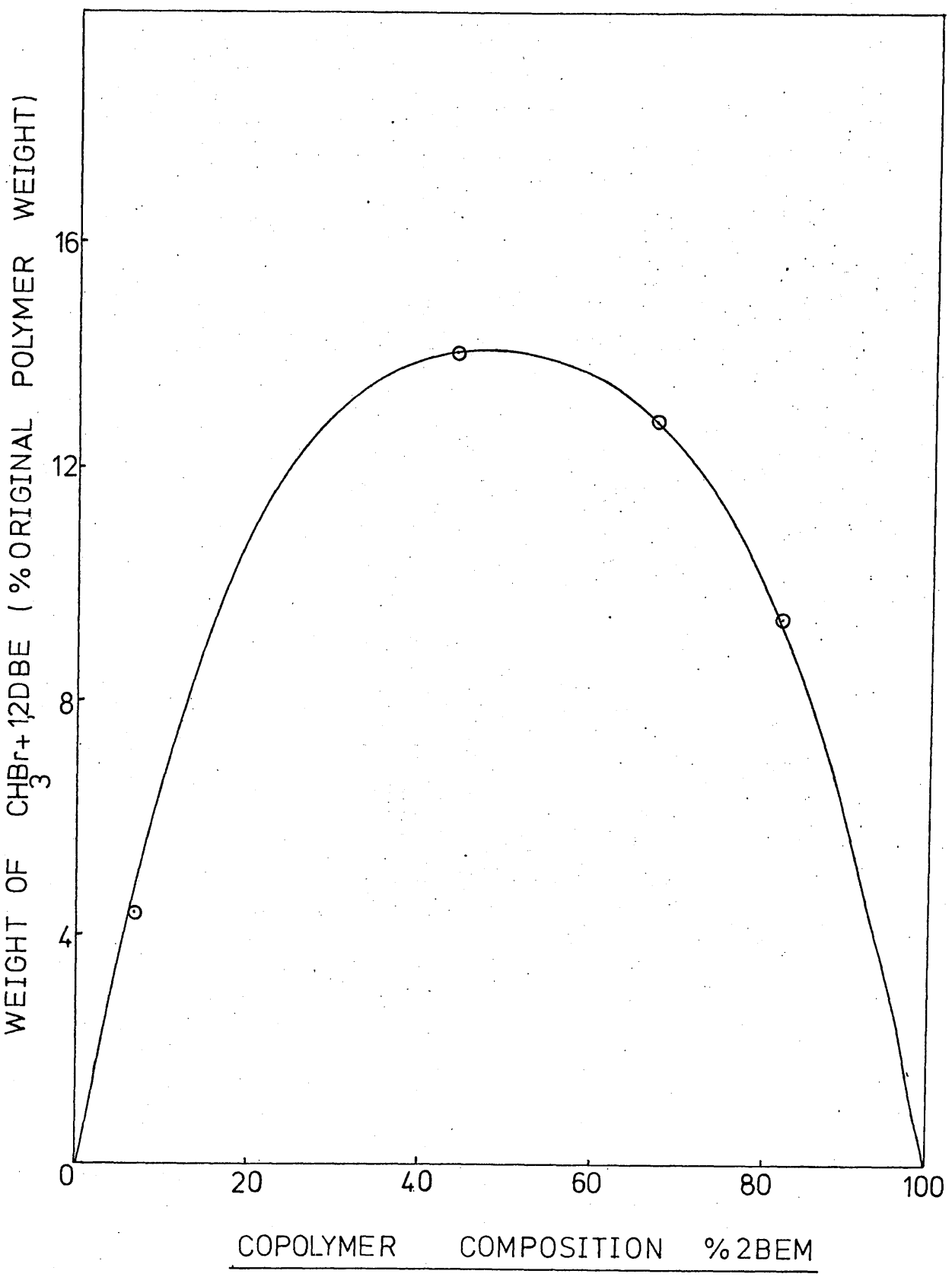


FIGURE 7.1 COMBINED WEIGHT OF METHYL BROMIDE AND 1,2,DIBROMOETHANE VERSUS THE COPOLYMER COMPOSITION

formed from competing abstraction and combination reactions of the common bromomethyl ($\bullet CH_2Br$) free radical. Figure 5.15 illustrates that these products are formed in the initial stages of volatilisation alongwith both monomers but were not associated with the formation of any other volatile product. From Table 5.7 it can be seen that methyl bromide production shows a maximum value of 12.5% of the original sample weight from copolymer A3 which approximates to a 1:1 system. This value represents 38% of the total bromine content in the copolymer.

The production of 1,2 dibromoethane on the other hand, decreases with increasing MA content from 7.2% in copolymer A1 to trace quantities in copolymer A4. The overall production of bromomethyl radicals however, does go through a maximum value at roughly a 1:1 copolymer monomer molar ratio as illustrated in Figure 7.1. This diagram illustrates the combined production of methyl bromide and 1,2 dibromoethane, expressed as a percentage of the original sample weight, as a function of the copolymer composition. The maximum of the curve lies in the composition region defined by 40-60% 2BEM units. Table 7.1 presents data on the sequence distribution of monomer units in the copolymers using a method developed by Harwood[73], which requires reactivity ratio values, monomer mixture and copolymer composition data. The first five columns in Table 7.1 are self-explanatory. The data in the last column represents the relative percentage concentrations of MA units in the middle of MA triads whose immediate environment is thus comparable with the environment of a MA unit

Copolymer composition 2BEM-MA %		2BEM-2BEM bonds in copolymer %	2BEM-MA bonds in copolymer %	MA-MA bonds in copolymer %	Fraction Z of MA in middle of MA triads	Z x % MA in copolymer
A1	81-19	64.8	32.4	2.8	0.022	0.42
A2	69-31	42.6	52.8	4.6	0.023	0.70
A3	48-52	19.1	57.8	23.1	0.197	10.3
A4	9-91	0.5	19.0	80.5	0.78	71.2

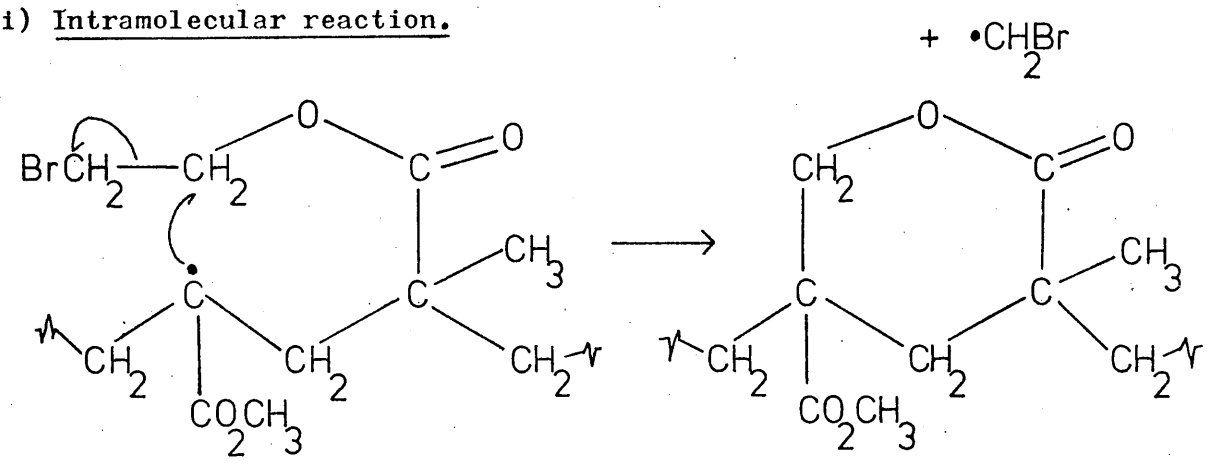
MAXIMUM NUMBER OF 2BEM-MA BONDS AT 45.3-54.7 COMPOSITION

TABLE 7.1 DATA ON SEQUENCE DISTRIBUTION IN COPOLYMERS A1 - A4.

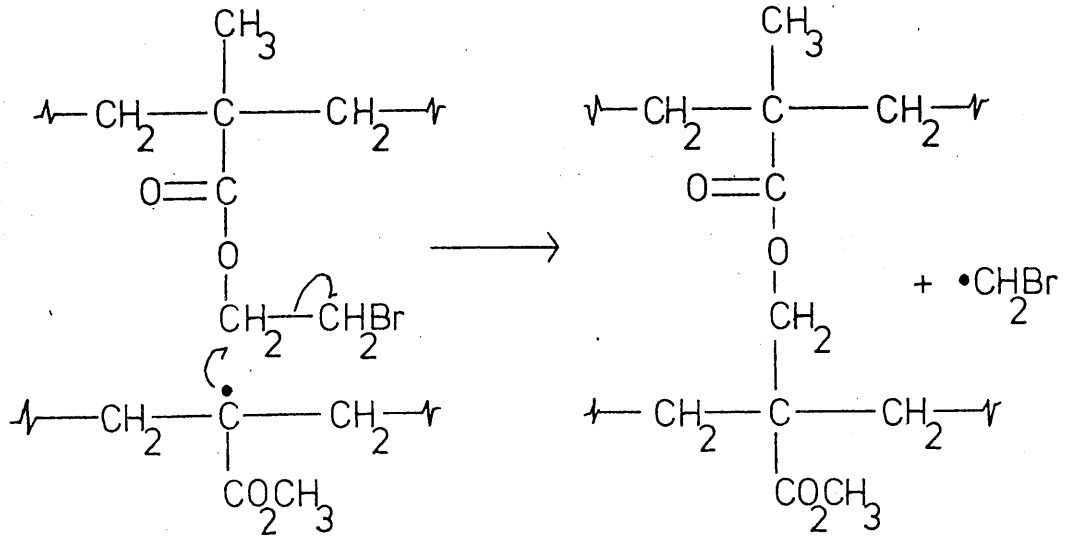
in a PMA molecule. This statistical method shows that the maximum number of 2BEM-MA bonds occurs at a copolymer composition of 45.3-54.7 2BEM-MA.

From this evidence it seems likely therefore, that the reaction giving rise to bromomethyl radicals is dependent upon the number of adjacent 2BEM-MA units in the polymer chain. This intramolecular reaction alone cannot however, account for the occurrence of methyl bromide and 1,2 dibromoethane among the degradation products of the 1:1 by weight blend system. In this case, an intermolecular reaction must take place giving rise to bromomethyl radicals. Possible reaction routes for the formation of bromomethyl radicals are shown below and originate from radical A which is thought to be formed very early in the degradation of the copolymers as discussed in the previous section on monomer production.

(i) Intramolecular reaction.



(ii) Intermolecular analogue.



This reaction involves radical attack of the acrylate polymer radical on the side chain of an adjacent 2-bromoethyl methacrylate unit displacing a bromomethyl radical and at the same time forming a six-membered lactone ring. The intermolecular analogue forms an ester crosslink structure. Molecular models suggest that the intramolecular process is sterically acceptable with the formation of a favoured six-membered ring structure. Such ring structures between adjacent units are formed during the degradation of many vinyl polymers, for example, anhydride structures from polymethacrylic acid,[17] imide structures from polyacrylamide and polymethacrylamide.[74] The six-membered lactone ring formed in the intramolecular reaction could be responsible for the broadening of the carbonyl region found in the polymer residue. The carbonyl absorption of the δ - lactone ring would lie in the region of 1750 - 1735cm^{-1} and may account for the observed shift of the carbonyl peak from 1725cm^{-1} in the undegraded polymer to 1745cm^{-1} in the residue after heating to 370^{o}C. The carbon-oxygen stretching frequency of this δ - lactone would be expected to occur at about 1160cm^{-1}. Figure 5.10 demonstrates that such an absorption occurs at 1150cm^{-1} in the 'cold ring' fraction from copolymer A2, supporting the existence of the δ - lactone ring system.

The intermolecular route produces an ester crosslink structure which satisfactorily accounts for the insolubility of the samples after minimal volatilisation. This reaction may also explain the occurrence of methyl bromide and 1,2 dibromoethane among the degradation products of the polyblend. In

that system, the intramolecular reaction cannot take place, and the amount of the two brominated volatiles is drastically reduced. This result however, cannot be used to interpret the extent of the intermolecular reaction in the copolymers as this reaction depends entirely on compatibility in the polyblend system. The copolymers are homogeneous and molecular mixing is more fully developed. Therefore, the relative importance of each process in the copolymer decomposition cannot be qualitatively estimated, although the fact that maximum production of these radicals coincides with the maximum number of A-B linkages suggests that the intramolecular process may be predominant.

The importance of the intermolecular reaction however, cannot be underestimated and may be particularly important at the extremes of copolymer composition when units of one monomer will be isolated in blocks of the other. The thermal breakdown products from these crosslinked structures may give an indication to the extent of this process and will be discussed later.

The bromomethyl radical produced from these displacement reactions will be relatively more stable than the methyl radical[75] and may undergo two possible reactions; namely combination with a similar radical to form 1,2 dibromoethane and hydrogen abstraction to form methyl bromide and a polymer radical. Table 5.7 shows that the combination reaction is favoured at low MA content, where the concentration of tertiary hydrogen atoms on the MA units is reduced. As the MA content increases, the abstraction reaction is favoured due to the increased availability of tertiary hydrogen atoms on the MA units. Hence, at a copolymer composition

of 9-91 2BEM-MA as present in copolymer A4, the abstraction reaction occurs to the complete exculsion of the combination reaction. Thus, the relative importance of the two possible reaction routes of the bromomethyl radical may be satisfactorily accounted for in terms of the availability of tertiary hydrogen atoms on MA units.

Further evidence for this displacement reaction mechanism is found in the spectroscopic analysis of the 'cold ring' fraction formed during degradation. Figure 5.13 shows a decrease in the absorption of the -C$\underline{H}_2$-Br protons relative to the -O-C$\underline{H}_2$- absorption. This indicates a general reduction of the number of-CH_2-Br groups in the chain fragments relative to other equivalent proton groups.

It seems therefore, that the bulk of the physical and chemical evidence supports these proposed intra-and intermolecular displacement reactions which give rise to both methyl bromide and 1,2 dibromoethane.

This displacement reaction is similar to, although not analogous to, that proposed by Cameron and Kane[57] to explain methanol production in PMA as discussed earlier. That reaction, however, involved polymer radical attack on a carbonyl group displacing a methoxy radical which in turn abstracts a proton to form methanol. In this copolymer system, the polymer radical displaces a bromomethyl radical to form a δ - lactone structure between adjacent units. The driving force for this reaction may not only be the formation of the stable δ - lactone ring system but also the stability of the bromomethyl radical,[75] the unpaired

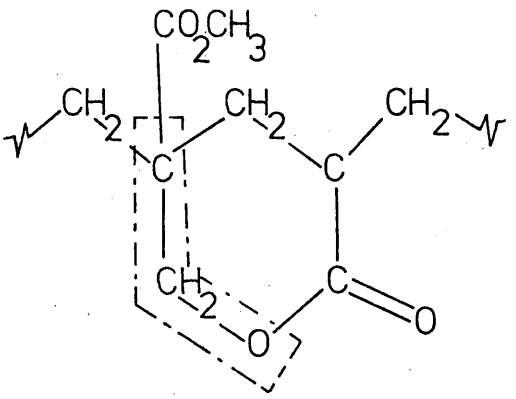
electron being delocalised to some extent by the bromine atom.

Considerations of the steric factors involved in this process show that the elimination of the alkyl group containing the bulky bromine atom is favoured. This reaction also reduces the steric interactions of the side groups by forming a stable six-membered ring system with a low steric energy factor. This reaction takes place once these polymer acrylate radicals are formed and explains the occurrence of methyl bromide and 1,2 dibromoethane among the initial volatiles evolved during degradation.

7.4 ACETALDEHYDE FORMATION

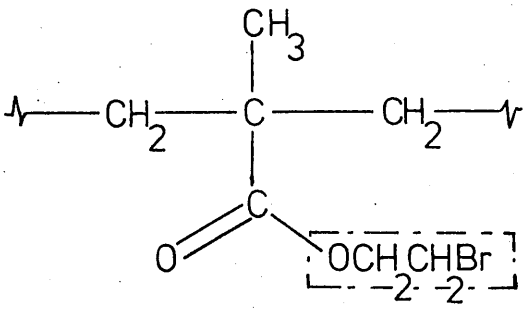
This compound is not found among the degradation products of either homopolymer. It is formed principally during the second stage of thermal decomposition of the copolymers in the temperature range 380 - 500°C, although some may be detected at lower temperatures. It is also found to a very small extent among the degradation products of the 1:1 polyblend system, again at elevated temperatures, in conjuction with ketene. Table 5.7 shows that the production of this product passes through a maximum value with changing copolymer composition. This suggests that the formation of acetaldehyde could be associated with a direct interaction of MA and 2BEM units, the greatest number of these interactions being possible at roughly a 1:1 monomer composition in the copolymer. It may also mean that acetaldehyde formation is associated with the breakdown of the structures formed during the bromomethyl radical formation reaction. The concentration of these

structures would also be greatest in the composition range 40 - 60% 2BEM. In order to form acetaldehyde from either the δ -lactone or crosslink structure however, at least three carbon-carbon bonds must be broken and three hydrogen atoms acquired. Although this product is found at elevated temperatures it seems unlikely



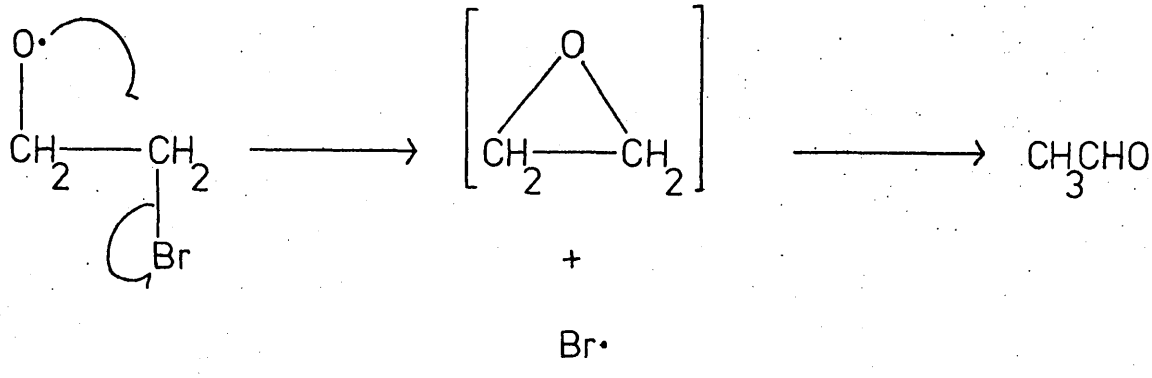
that such a complex reaction sequence could occur. The other possible two carbon unit which may give rise to acetaldehyde is the bromoethyl group of the methacrylate monomer.

In this instance, the bromine atom would have to be removed



as well as an intramolecular rearrangement. If however, a

radical such as the brominated alkoxy radical was formed then a dehalogenation reaction may take place to form ethylene oxide which may then rearrange to acetaldehyde at degradation temperatures:-



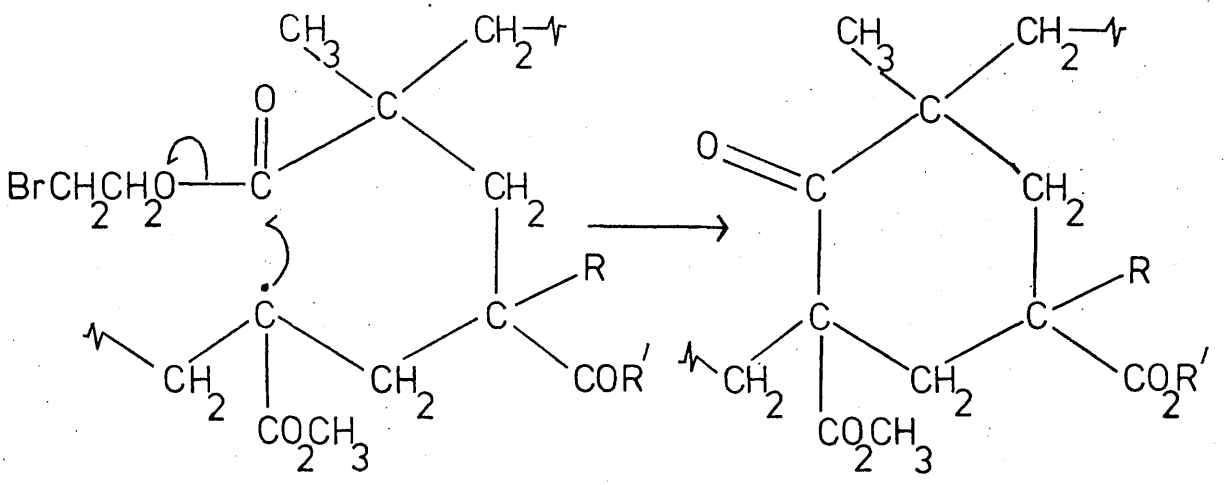
The formation of ethylene oxide by this cyclisation process was first carried out in 1859 by Wurtz[76] who produced ethylene oxide by heating 2-chloroethanol in the presence of potassium hydroxide. This expoxidation reaction eliminates free bromine atoms, which may explain the occurrence of small amounts of HBr and Br_2 among the degradation products of the copolymers. Mueller and Walters[77] studied the thermal decomposition of ethylene oxide and found that in the temperature range 380-500°C acetaldehyde, ketene and small amounts (about 1%) of formaldehyde were formed. These workers also studied the effect of propylene, a free radical scavenger, on this reaction and showed that acetaldehyde production was enhanced with a corresponding decrease in ketene formation. This result agreed with the findings of

Fletcher and Rollefson[78] who concluded that some proportion of the isomerisation reaction takes place via a free radical route. The ketene reaction is thought to involve a reaction between a free radical and ethylene oxide molecule to produce ketene without concurrent loss of hydrogen.

In order to test whether the above reaction sequence occurs in the copolymer system being studied, a model polymer poly 2-bromoethyl acrylate (P2BEA) was prepared as described in Chapter 2. According to Grassie and co-workers[18] the thermal degradation of poly(n-alkyl acrylates) produces condensable volatiles identified as the corresponding alkyl alcohol and carbon dioxide. In P2BEA therefore, 2-bromoethanol and carbon dioxide would be expected to be among the condensable volatile fraction. It was found that the decomposition products of P2BEA (see Appendix 2) consisted mainly of chain fragments, acetaldehyde and carbon dioxide. Acetaldehyde production was found to amount to 23% of the original weight which is comparable with ethanol production 22.4% from poly(ethyl acrylate) as found by Grassie et al.[18] There were also minor amounts of HBr and Br_2 detected from P2BEA.

Assuming that in the P2BEA system the brominated alkoxy radical is formed in the same manner as the analogous n-alkyl alkoxy radical in these other acrylate polymers, then it would seem that this brominated alkoxy radical does undergo these dehalogenation and isomerisation reactions to form acetaldehyde with elimination of a bromine atom. This reaction route therefore would explain the occurrence of acetaldehyde in both the copolymer and blend systems.

The mechanism for the production of this brominated alkoxy radical may be analogous to that proposed for alcohol formation in the poly n-alkyl acrylate case, namely, chain MA radical attack on the carbonyl group of a 2BEM group two units along the chain:-



R = H or CH_3

R′ = CH_3 or CH_2CH_2Br

to form a saturated six-membered β - keto ester. The corresponding intermolecular reaction gives rise to a similar acyclic structure. The saturated ketone would absorb in the 1700-1720cm^{-1} region in the infra-red which might explain the broadening of the carbonyl absorption to lower frequencies with a pronounced shoulder at 1700 cm^{-1} as found in both the residue and 'cold ring fractions from the second stage of copolymer degradation. The fact that acetaldehyde production takes place in a similar temperature range (about 400^{o}C) as

alcohol formation in the poly(n-alkyl acrylate) polymers supports the above proposal.

An alternative source of these brominated alkoxy radicals may be from simple acyl-oxygen bond scission of isolated 2BEM units trapped in the copolymer and exposed to temperatures greater than those at which depolymerisation normally occurs. Ester decomposition takes place, however, even to a small extent in the homopolymer and would be expected to occur preferentially to acyl-oxygen scission at these higher temperatures.

As with methyl bromide formation, it is difficult to estimate the relative importance of the intra-and intermolecular processes. The formation of acetaldehyde and ketene in the polyblend system indicates that the intermolecular process does take place. However, the quantitave information presented in Table 5.7 suggests that as the production of this compound is dependent on copolymer composition, the maximum amount being produced at roughly 1:1 monomer composition, the intramolecular process may predominate.

Further evidence for the production of acetaldehyde via ethylene oxide is the detection of very small amounts of this intermediate among the degradation products by gas-phase infra-red spectroscopy. At degradation temperatures this intermediate will almost exclusively isomerise to form acetaldehyde. However, under continuous pumping conditions some may volatilise before subsequent rearrangement can occur.

The formation of the brominated alkoxy radical receives further support from the fact that 2-bromoethanol is found

among the condensable volatiles of each copolymer. As shown in Table 5.7 the production of this compound decreases with increasing MA content. It seems therefore, that hydrogen abstraction by the brominated alkoxy radical becomes increasingly difficult with greater concentrations of MA units. This surprising trend may be explained by considering the physical nature of the degradating polymer sample and the fact that this product was not detected among the products of thermal degradation of P2BEA (see Appendix 2). It seems that the higher the MA content the lower the possibility of radical diffusion to enable transfer reactions to occur. This reduction in polymer flexibility is due to the gel formation which becomes increasingly important with increasing MA content, and is a general feature of acrylate degradation.[18,55] The brominated radicals are then forced to undergo rearrangement before abstraction is possible. At higher methacrylate content, gel formation is not sufficiently advanced to prevent radical diffusion leading to alcohol formation. This explanation for 2-bromoethanol production however, must be regarded as highly speculative since no systematic investigation of chain flexibility, in isolation, on reactions in polymers has been reported.

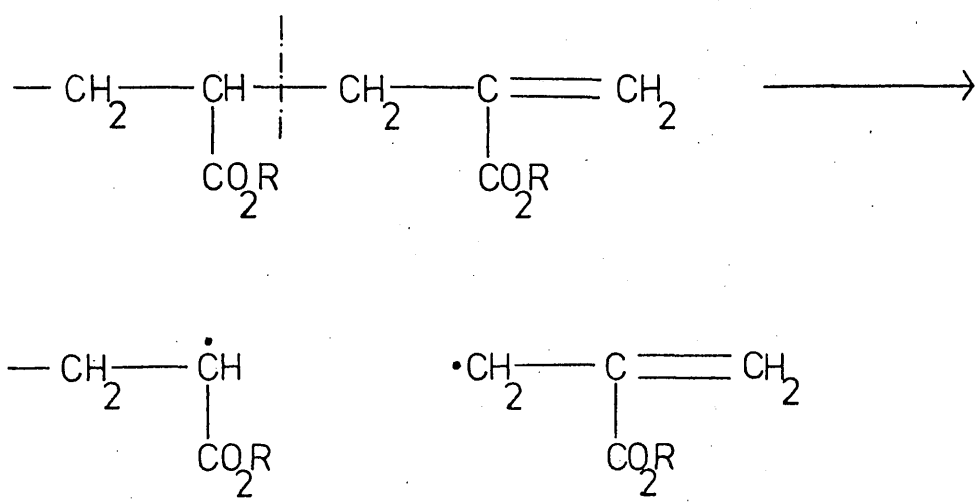
The small amounts of ketene found in both the copolymer and polyblend systems were thought to be associated with the production of acetaldehyde. This compound is found as a product of thermal decomposition of ethylene oxide.[77] It is thought to be formed by a radical interaction of ethylene oxide which does not give rise to hydrogen. As the production

of ketene relative to acetaldehyde was found to be greater in the blend system, which did not produce substantially high amounts of hydrogen, this evidence would seem to support the above conclusion.

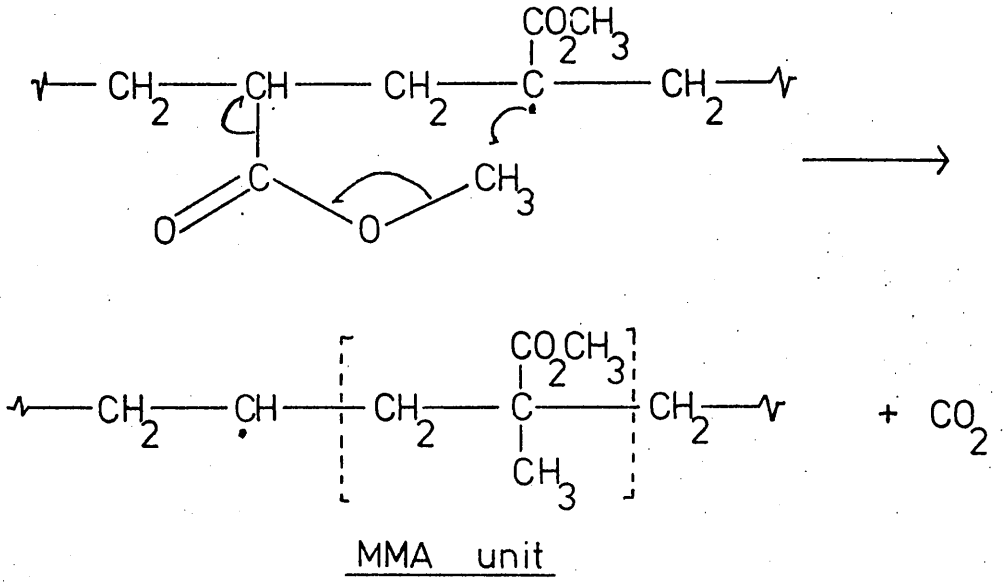
Thus, all of the evidence presented suggests that acetaldehyde production in both the copolymer and blend systems may be explained by intra-and intermolecular radical displacement mechanisms to produce a brominated alkoxy radical which undergoes a dehalogenation reaction to form ethylene oxide which in turn isomerises at degradation temperatures to form acetaldehyde. 2-bromoethanol may be formed from the alkoxy radical by hydrogen abstraction at high methacrylate content, while ketene is produced from an alternative decomposition process of ethylene oxide which may involve a radical interaction.

7.5 METHYL METHACRYLATE PRODUCTION

Although this compound is found among the decomposition products of PMA[18,57] it is produced in greater quantities in the copolymer and blend systems than may be expected on the basis of MA content alone. The presence of traces of the corresponding methacrylate monomer among the degradation products of a series of poly (n-alkyl acrylates) was explained in terms of chain-end reactions:-[18]

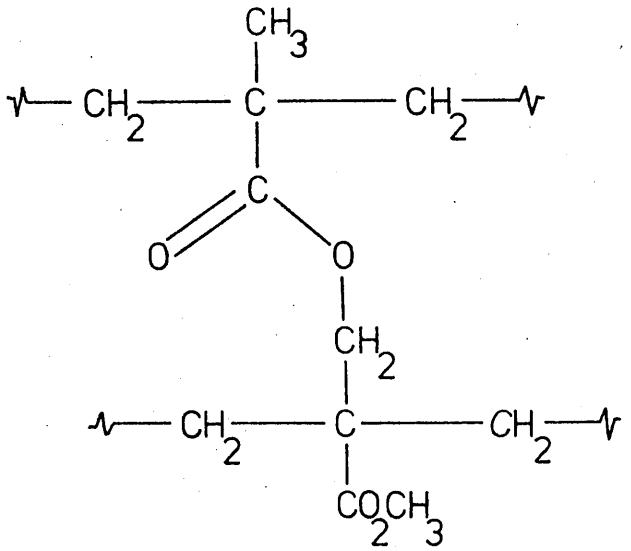


Cameron and Kane[57] proposed the following mechanism to explain carbon dioxide and methyl methacrylate formation in PMA:-

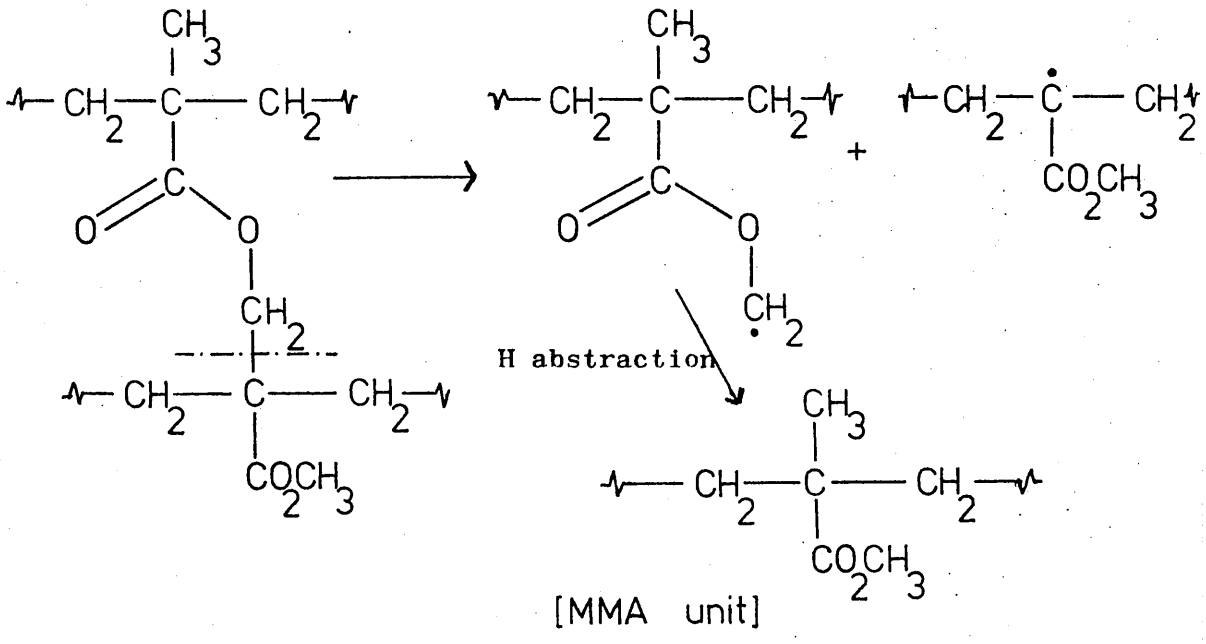


MMA unit

MMA is produced from both degradation stages in the copolymer system although the relative proportion arising from each stage was not quantitatively investigated. Qualitative information however, suggested that this product was produced chiefly during the second stage of decomposition. The substantial production of MMA from the 1:1 blend system led to the proposal that this compound is directly associated with the decomposition of the crosslink structures formed from the intermolecular methyl radical displacement reaction which occurs exclusively in the polyblend system. This reaction creates a crosslink structure shown below:-

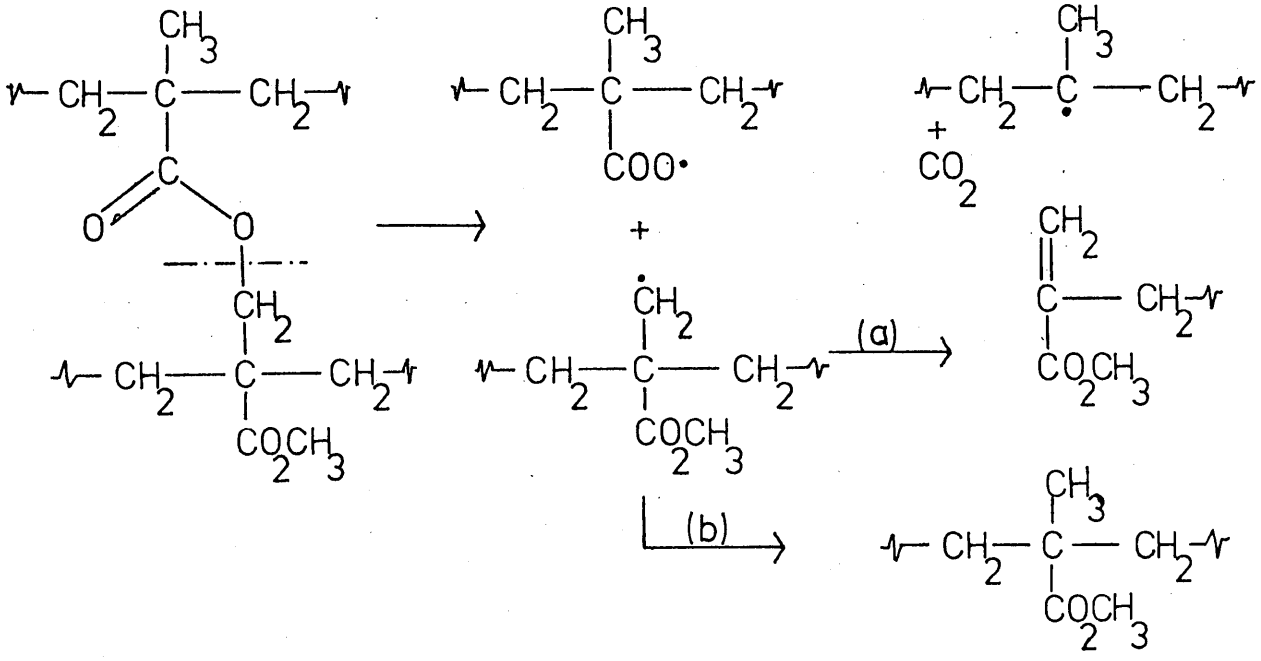


which may thermally decompose by two possible mechanistic pathways to produce MMA units in the polymer chain. The first mechanism involves subsequent scission of the carbon-carbon bond which was originally formed in the displacement reaction.



This regenerates the polymer acrylate radical and a methyl methacrylate type radical which may abstract a hydrogen atom to form a MMA unit in the chain.

The second route may originate from carbon-oxygen bond scission to produce a carboxy radical and a methylene radical on a MMA unit.



The carboxy radical would most likely undergo decarboxylation followed by chain scission of the polymer radical, a process first suggested by Grassie and Torrance.[59] The methylene radical on the other hand has two possible routes to MMA formation. The first involves the formation of an unsaturated chain-end structure via chain scission. The alternative hydrogen abstraction reaction would again form a MMA unit in the polymer chain.

It is to be noted that each MMA forming mechanism ultimately requires the acquisition of a hydrogen atom. The second mechanism however, leads to concurrent loss of a carbon dioxide molecule. As carbon dioxide can be formed in a number of ways this does not aid elucidation of the MMA forming reaction although concurrent production of both species is evident in both systems. Table 5.7 shows that production of MMA increases with MA content. This trend may be due to a simple increase of MMA from MA units or because the intermolecular methyl radical displacement reaction becomes more important at higher MA content. The fact that the amount of MMA produced is greater than can be expected from the MA content alone supports the latter explanation of MMA formation.

It is not possible, from the evidence presented, to say which scission process occurs in the degrading copolymer, although carbon-oxygen scission would seem to be the more likely on the basis of bond dissociation energies and the fact that a gaseous carbon dioxide molecule would be released concurrently.

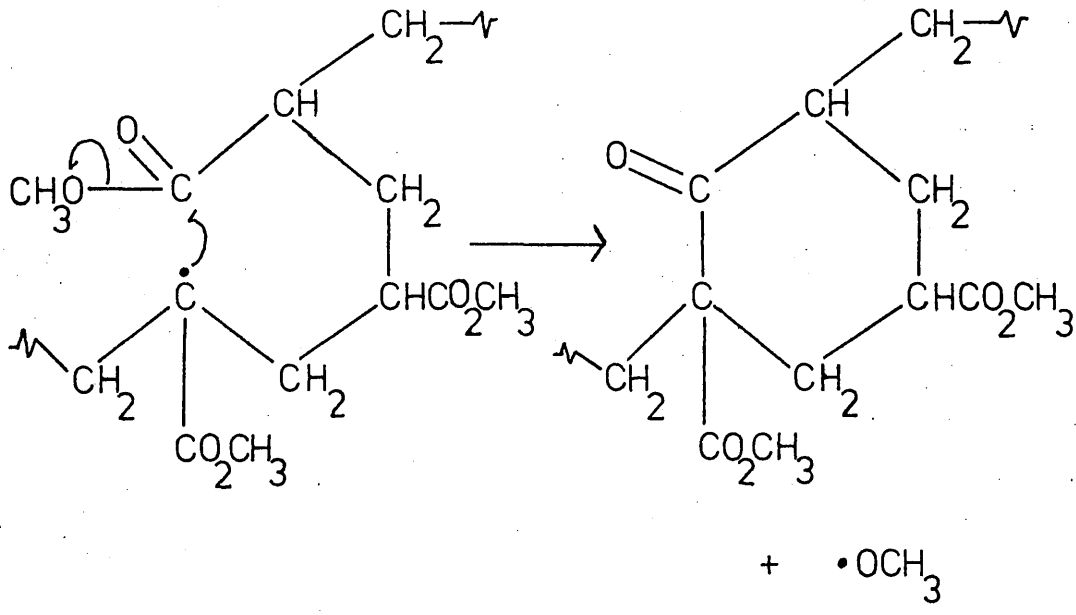
An analogous reaction to the decomposition of crosslink structures to form one specific compound has not been previously

reported. However, it is difficult to see how the formation of this product, especially in the blend system, may be satisfactorily explained in any other manner.

7.6 METHANOL PRODUCTION

Methanol is formed exclusively in the second stage of degradation in the temperature range 380-500°C in both the copolymer and blend systems. As Table 5.7 demonstrates it is not detected from copolymer A1 which contains the lowest MA content, but increases in importance with increasing MA content. It would appear therefore, that methanol production is a property of sequences of MA units and not of isolated units. This production trend may be rationalised by considering the information on sequence distribution presented in Table 7.1 using Harwood's methods.[73] The data in the last column represents the relative percentage concentrations of MA units in the middle of MA triads whose immediate environment is equivalent to that found in a PMA molecule. Comparison of quantitative production of methanol with sequence distribution information suggests that methanol production is a property of sequences of at least three MA units. This result is in accord with the conclusions of Grassie and Torrance[58] who found no methanol among the thermal degradation products of copolymers of MMA-MA with high methacrylate content. These workers did not detect methanol even from a 2:1 MMA-MA composition. In this present study, methanol was found at about this ratio, but only to a very small extent. The occurrence of this reaction is therefore dependent on the sequence distribution of both the monomer units which in turn

is a function of the reactivity ratios. In this case the larger difference in reactivity rarios means that longer sequences of MA units are present in 2BEM-MA copolymers of equivalent composition to MMA-MA copolymer. Thus, methanol production should be expected from 2BEM-MA copolymers with lower MA contents. The mechanism of this reaction is thought to be analogous to the methanol formation reaction which takes place in PMA[57] as described in an earlier section. This reaction is possible, as the presence of the polymer acrylate radical required to produce the displacement reaction, has already been established:-



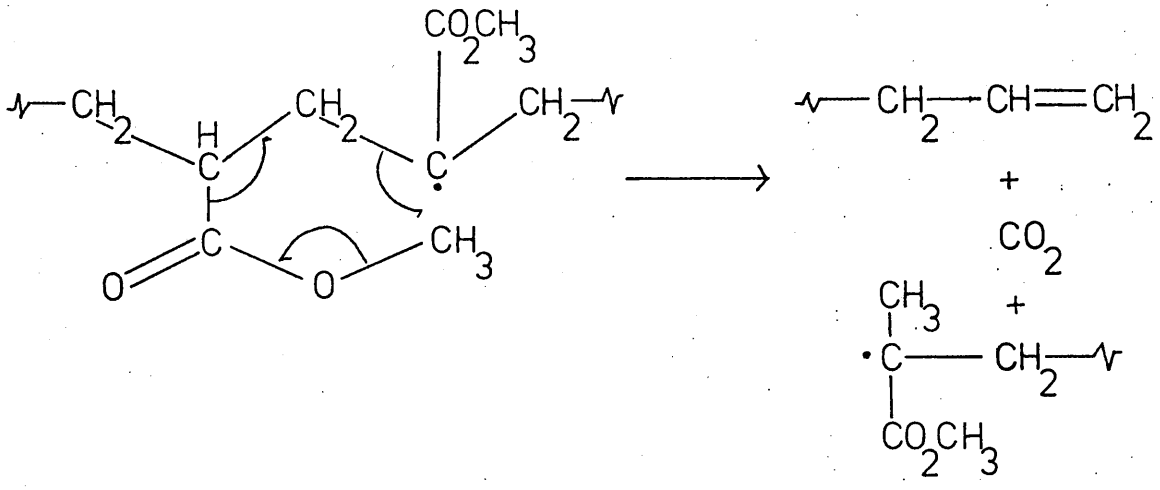
This displacement reaction, which may also occur intermolecularly, only takes place at temperatures at which PMA itself decomposes, yet it has been suggested that this polymer acrylate radical is present during the first stage of degradation, being responsible for methyl bromide and 1,2 dibromoethane formation.

This evidence suggests that the energy required for the production of the methoxy radical is greater than that needed to form the bromomethyl radical. The reason for this situation may lie not only in the relative stability of the radicals which are produced from either reaction but by the fact that methanol requires the interaction of three consecutive MA units, whereas adjacent MA-2BEM units can interact to form a bromomethyl radical. Hence, the former process occurs only at temperatures at which segmental motion of the chain is such that a 1,3 interaction may take place, whereas interaction of adjacent units is possible at much lower temperatures. As in the thermal degradation of PMA it is not possible to estimate the relative contributions to methanol formation from the two displacement mechanisms, although the intramolecular reaction is thought to predominate in the homopolymer.[57]

7.7 CARBON DIOXIDE PRODUCTION

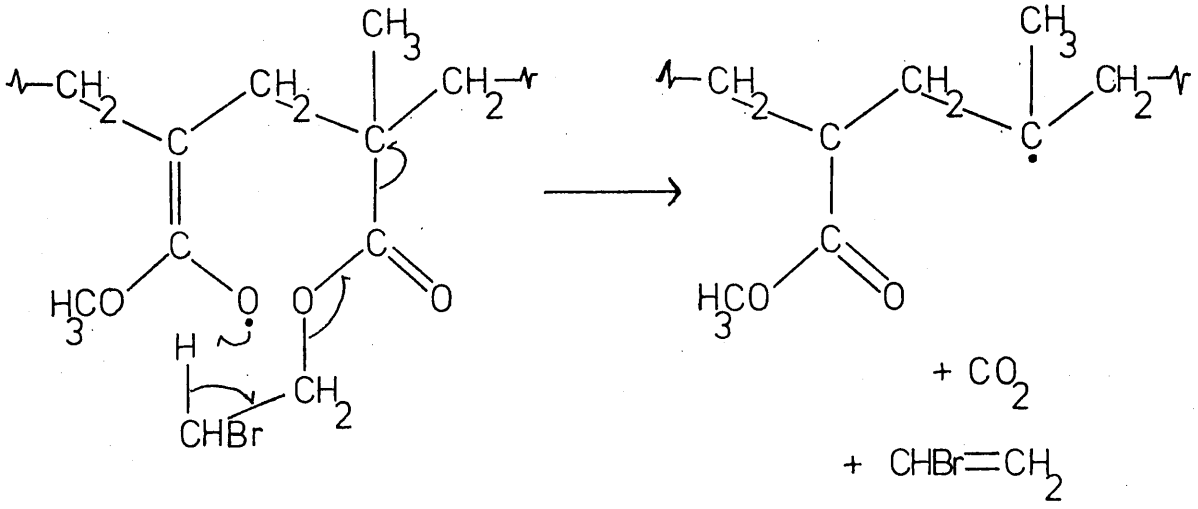
This compound is formed during both stages of degradation of both the copolymer and blend systems. It is not formed at the very early stages of copolymer volatilisation, however, being primarily evolved at temperatures above 360°C. It is a product common to both homopolymers, although P2BEM produces only trace amounts which are due to ester decomposition of the side group. Table 5.7 presents the qualitative information on the production of this gas from each copolymer. There is an obvious trend of increasing formation of this product with increasing MA content. When this data is presented as a weight percentage of the original MA content of each copolymer the opposite trend

prevails. This may mean that either the carbon dioxide formation reaction becomes increasingly important whenever MA units become isolated or that there is some other mechanism of formation of this compound in the copolymer system. Grassie and Torrance[58,59] on the basis of their quantitative results from copolymers of MMA-MA concluded that liberation of carbon dioxide is not only a property of individual MA units but that it is associated with chain scission. They suggested a mechanism similar to that first proposed by Fox and his colleagues[62], which involves the shift of an alkyl group.



This reaction may however, be thought to become less likely as the size of the alkyl group increases.

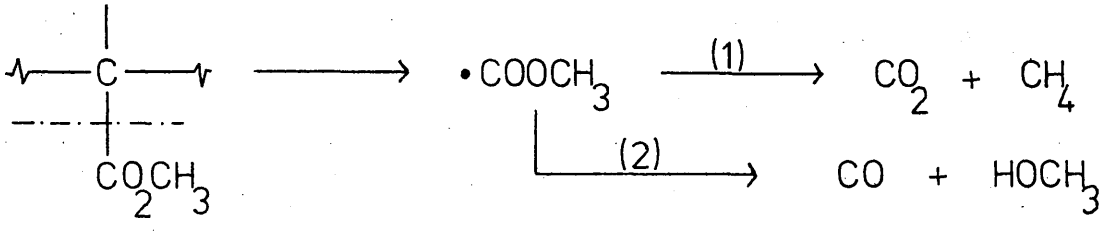
An alternative reaction may be similar to that proposed by Grassie et al[18] which involves the resonance stabilised form of the polymer radical resulting from intermolecular transfer.



This reaction results in concurrent loss of vinyl bromide, which only appears in very small quantities. This route, therefore, may only make a small contribution to total carbon dioxide production.

As discussed earlier, carbon dioxide may be a direct result of thermal decomposition of the structures formed in the bromomethyl radical formation reaction. This leads to concurrent production of MMA units from both the δ - lactone and crosslink structures. These units may however, not all volatilise as MMA monomer, some being trapped as part of the chain fragments, so that the amounts of MMA produced would be very much less than the carbon dioxide production from the same source.

Carbon dioxide may also be formed during the latter stages of degradation by decomposition of the ester side chain to yield the methyl formate radical which could decompose to give carbon dioxide and a methyl radical.



An alternative decomposition of this radical to give carbon monoxide and methanol is also possible. No methyl formate was detected among the degradation products, however,

and the contribution of this mechanism to the carbon dioxide yield may be minor.

It would seem from the quantitative data that the production of carbon dioxide may originate from a number of reaction routes. The relative importance of each route however, cannot be accurately estimated, although it would seem that those involving MA units become increasingly important as the MA content of the copolymer is increased. The most likely alternative source for this gas would seem to be the decomposition of the δ - lactone and crosslink structures formed during the bromomethyl radical displacement reaction. The presence of vinyl bromide among the condensable products also suggest that some contribution must come from the ester decomposition route.

7.8 MINOR DEGRADATION REACTIONS

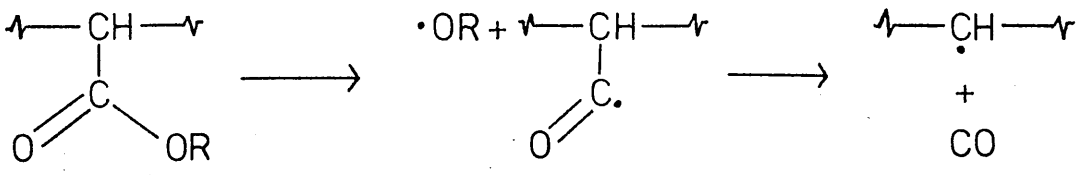
Vinyl bromide is found among the degradation products from each of the copolymers but was found to be absent from the decomposition products of the blend. The formation of this compound in trace amounts in P2BEM was attributed to the ester decomposition reaction of the brominated side-chain. In the copolymer system it seems likely that vinyl bromide originates from the decomposition of isolated 2BEM units which are exposed to temperatures at which depolymerisation normally occurs.

The occurrence of hydrogen bromide and bromine has already been discussed in terms of the two competing abstraction and combination reactions of the free bromine atom formed during the acetaldehyde formation reaction.

As the MA content of the copolymer increases, the chain fragments collected at the 'cold ring' fraction become more

intensely coloured. Figure 5.12 shows the general increase in absorption in the ultra-violet region 2750-3550 Å, and there is a corresponding peak at 1630cm^{-1} in the infra-red spectrum which is due to carbon-carbon double bond absorption. From this evidence it is presumed that the colour is the result of conjugation involving principally carbon-carbon double bonds, but possibly also carbonyl groups. The formation of this colour has been explained in the section dealing with PMA, in terms of elimination reactions along the polymer backbone producing products such as hydrogen and methane. This colouration is observed in the early stages of degradation and is again associated with the methyl acrylate chain radical which has been shown to be present at these low temperatures. These conjugated sequences do not appear to run to great length as there is no obvious bathochromic shift as degradation proceeds. This reaction may also account for the production of non-condensable species such as hydrogen and methane which are produced in the first stage of degradation of each of the copolymers and detected by TVA.

Carbon monoxide was found to be the principal non-condensable product from the latter stages of degradation and may be associated with the decomposition of the saturated ketone and δ - lactone structures which are formed in the methanol and methyl bromide reactions respectively. It may also be derived from acyl-oxygen scission to give a carbonyl radical which is very unstable[67] and will decompose immediately to give carbon monoxide.



7.9 CONCLUSIONS

The foregoing discussions of the possible mechanisms of formation of the various products from the the thermal degradation of 2BEM-MA copolymers allow the following integrated reaction sequence to be drawn up (volatile products are underlined) as shown in Figure 7.2.

The evidence favours random scission in reaction (1) rather than chain-end initiation. The interplay of reactions (3), (4) and (5) ultimately determines the principal characteristics of the overall reaction. If the terminal MA radical resulting from reaction (2) is isolated, as is predominantly so in copolymer A1, then reactions (3) and (5) assume greatest importance. When the MA content is increased such that MA units occur increasingly in groups then reaction (4) becomes significant and by comparison with reaction (5) proves to be much faster than reaction (3). It is the relative concentration of the MA chain radicals produced from reaction (4) which determines the overall production of each of the volatiles. This chain radical may undergo a number of competing radical side processes such as elimination, displacement and chain scission to give rise to the various fractions and products of degradation.

At lower temperatures, in addition to depolymerisation, this MA chain radical is involved in reactions of the type (6), (7) and (8) whereas at elevated temperatures reactions (9) and (10) become increasingly important.

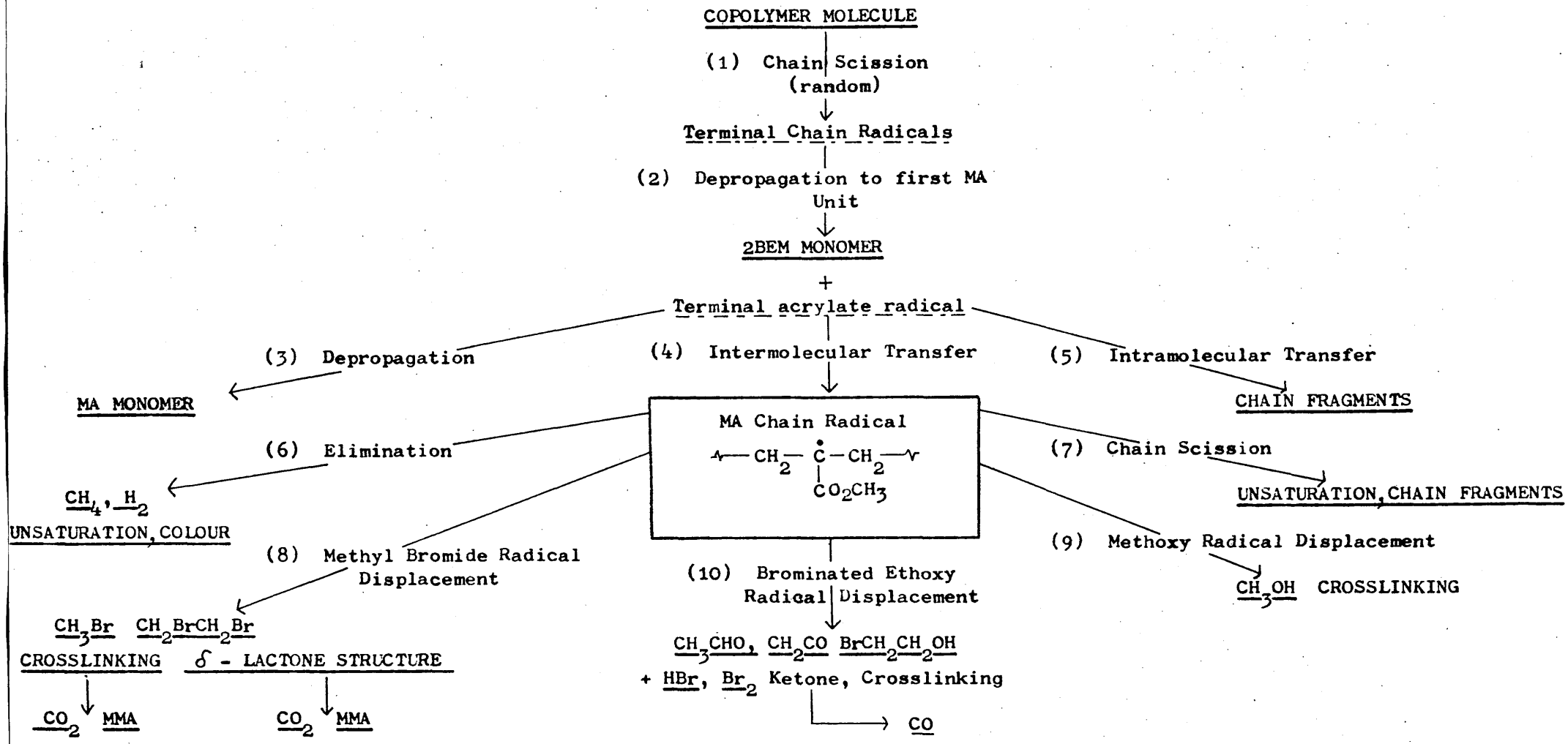


FIGURE 7.2 PROPOSED REACTION SEQUENCE FOR DEGRADATION OF 2BEM/MA COPOLYMERS.

These displacement reactions (8), (9) and (10) have also been shown to occur at phase boundaries in the 1:1 polyblend system. Reactions (8) and (10) involve the interaction of two different monomer units and show a maximum importance at copolymer compositions in the range 40-60% 2BEM-MA, at which the maximum number of A-B linkages also occurs. Thus, these displacement reactions are thought to occur predominantly by an intramolecular mechanism although evidence of the intermolecular process is provided by the polyblend system.

CHAPTER 8

THERMAL DEGRADATION OF A 2-BROMOETHYL METHACRYLATE - STYRENE COPOLYMER

8.1 INTRODUCTION

This chapter deals with the thermal degradation behaviour of an approximately 1:1 copolymer of 2BEM and styrene. Copolymers containing these two monomer units have previously been synthesised by Luskin and Myers,[35] who determined the reactivity ratios for this pair of vinyl monomers. They did not, however, report on the thermal stability or decomposition products of this copolymer system.

It has been shown in the previous chapter that the thermal degradation behaviour of 2BEM units can be greatly influenced by the presence of MA groups in the polymer chain. In PMA, transfer reactions predominate to give mainly chain fragments, monomer being produced only in trace quantities. The degradation of PS, on the other hand, involves both depropagation and transfer reactions with

monomer constituting 42% of the original sample weight.[79] Its thermal degradation behaviour therefore, is intermediate between that of PMMA on the one hand which unzips exclusively and PMA, on the other, in which transfer reactions predominate. A copolymer of 2BEM and styrene was therefore studied, in order to determine whether any interaction between the monomer units takes place during the degradation process.

Although the thermal breakdown behaviourof 2BEM/S copolymers has not been previously investigated, Grassie and Farish[72] have studied the related MMA/styrene copolymer system and their results have been compared with those from the halogenated system.

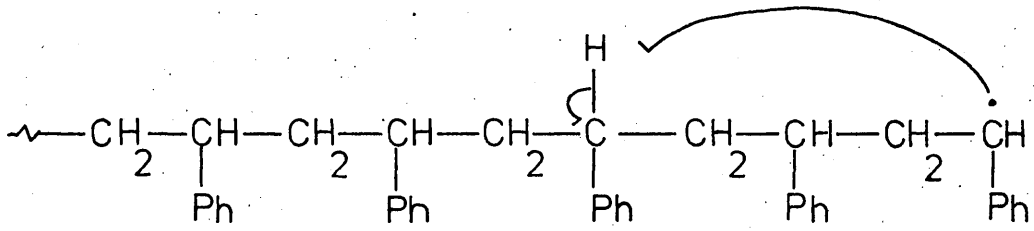
A brief account of the thermal decomposition of PS will be followed by the results and discussion of the degradation of the 2BEM/S copolymer system.

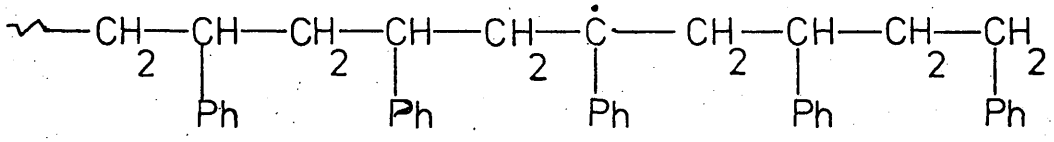
8.2. DEGRADATION OF POLYSTYRENE

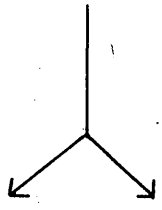
The thermal degradation characteristics of polystyrene have received a great deal of attention over the years and yet the interpretation of experimental data is still the subject of controversy. Cameron and McCallum[80] have comprehensively reviewed all of the work related to this problem up to 1967. Although there is general agreement on a number of points relating to the nature of the degradation products and their mechanism of formation, there has however, been continuous speculation over the interpretation of the rapid decrease in the molecular

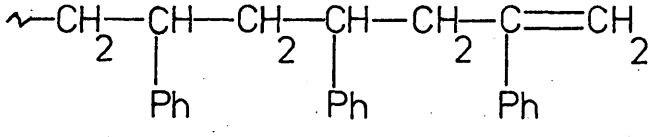
weight which occurs early in the reaction and in particular whether it is due to 'weak links' in the polymer chain or to intermolecular transfer.

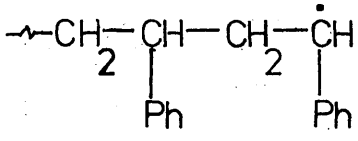
Styrene monomer constitutes 42% by weight of the original polymer, with progressively decreasing amounts of dimer, trimer, tetramer and pentamer and small amounts of toluene and benzene. On the basis of the nature and distribution of such products a mechanism of degradation has been proposed involving both intra-and intermolecular transfer reactions in addition to simple depolymerisation. Grassie and Kerr[81] have shown this monomer to non-monomer ratio to be constant throughout decomposition and that this can only be explained in terms of depropagation of the initially formed terminal polymer radical accompanied by intramolecular chain transfer as illustrated below. The importance of transfer processes during the degradation of polystyrene is underlined by experiments on poly(α-deuterostyrene)[82] which exhibits an isotope effect with the monomer yield increasing to 70% by weight of the original sample. The relative importance of the intermolecular transfer step is however, a point of contention. Wall et. al.[83] suggest that all the degradation products may be accounted for assuming intermolecular transfer alone. If this were the case then the ratio of monomer to non-monomer would be expected to diminish with volatilisation. Results to the contrary have been repeated, however, by Grassie and Kerr[81] and Makorsky and Straus.[79] Nevertheless, a radiochemical study by Richards and Salter[84] has established the existence of an intermolecular











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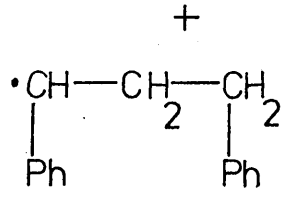
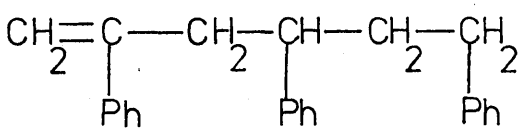


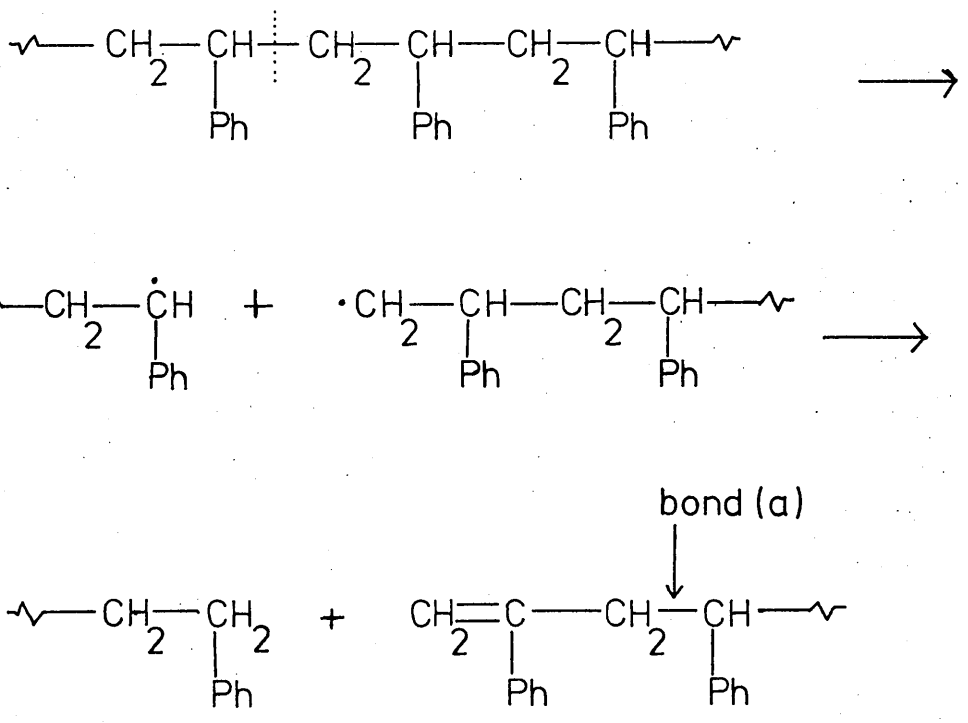
dimer radical



trimer molecule

transfer step among the pyrolysis reactions.

There is general agreement that initiation is chain terminal because the rate of depolymerisation is strictly proportional to the number of chain-ends in the degrading polymer.[83] In order to rationalise the apparent increase in chain-end concentration with degree of volatilisation Grassie and Kerr[81] proposed the existence of a radical 'cage' which deactivates the radicals produced from random chain scission by recombination or more likely disproportionation. This 'cage' effect may also explain the absence of unzipping following random chain scission:-



Bevington et al[71] have shown that a combination termination reaction occurs almost exclusively during PS polymerisation, so that no unsaturated chain-ends exist in undegraded polystyrene prepared by free radical methods. The above reaction would produce such unsaturated structures which

would undergo scission at the labile bond (a) to give the active primary radical.

A study of the thermal degradation characteristics of a number of polystyrene samples prepared by radical and anionic routes by Cameron and Kerr[85] provides good evidence for the existence of 'weak links' in the radically prepared polymers. These workers showed that polystyrenes prepared using an anionic initiator are free from 'weak links'. On the other hand, scission at 'weak links' is superimposed on the normal random scission process in radical initiated polystyrenes. Cameron and Kerr[86] concluded that the 'weak links' are most likely to be oxygenated groups, probably peroxide links which have become incorporated into the polymer during its preparation. They were unable to prove this unequivocally, however.

The mechanism of thermal degradation of radically prepared polystyrene can be explained therefore, in terms of a depolymerisation reaction initiated at chain-end structures with concurrent radical transfer processes which occur by a predominantly intramolecular route to give rise to the various oligomer fragments.

8.3 RESULTS

(a) Thermogravimetry and TVA

Both the weight loss curve and the TVA thermogram for polystyrene are shown in Figure 8.1. From this superposition of data it is evident that weight loss is concurrent with the production of volatiles condensable at ambient temperatures.

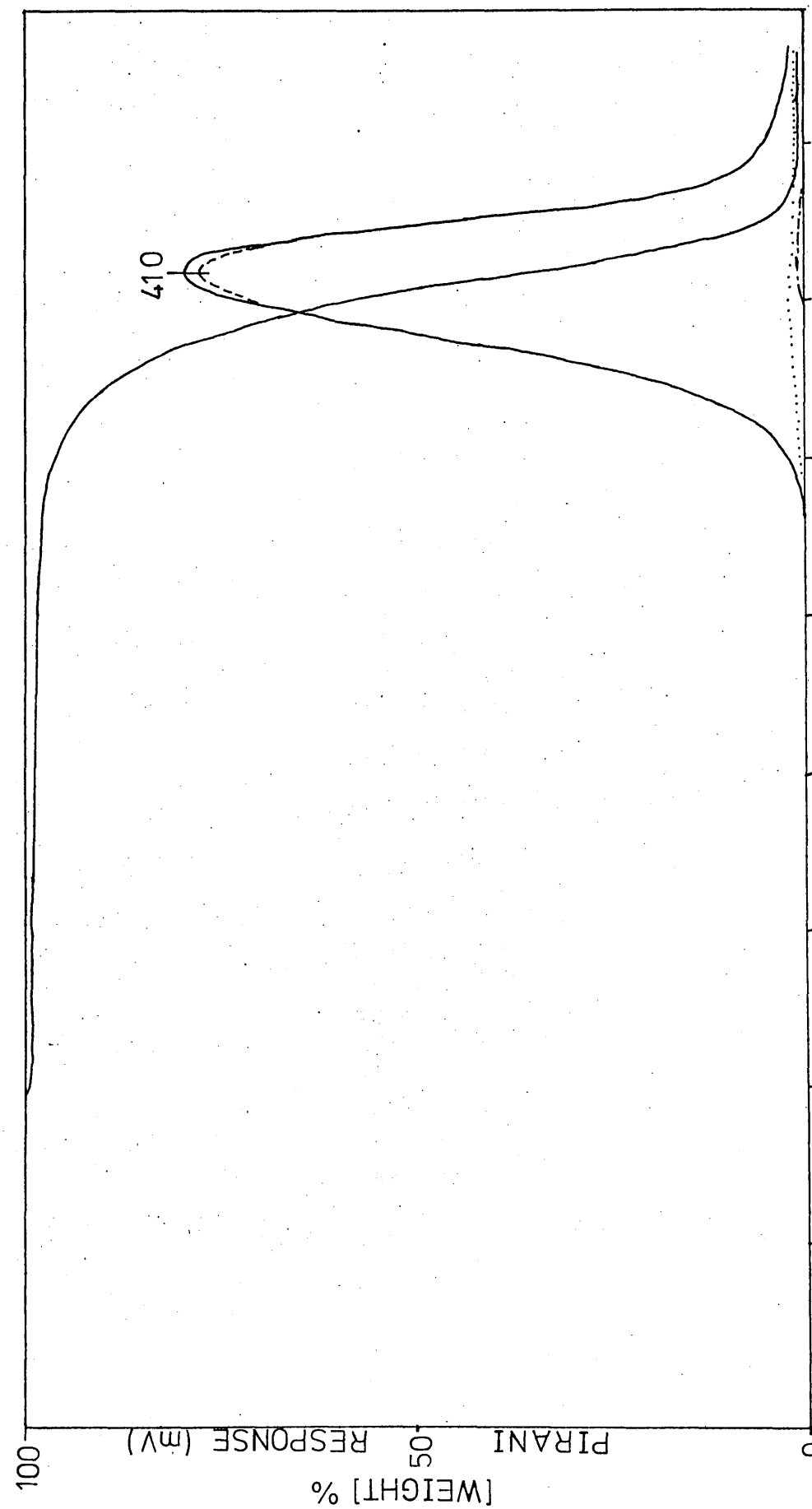


FIGURE 8.1 TVA TRACE OF POLYSTYRENE POWDER (54 mgs) AND WEIGHT LOSS CURVE FROM THERMOGRAVIMETRY.

Thermogravimetry shows a single stage reaction which is completed by 430°C and accounts for 99% of the original weight. Volatilisation begins at approximately 315°C and reaches a maximum rate at 405°C.

A single stage process can also be discerned from the TVA profile of condensable species. These products begin to be evolved at about 325°C and reach a maximum rate at a temperature (T_{max}) of 410°C. The profile is due to the co-incident 0°C and -45°C traces with the -75°C trace exhibiting a small limiting rate effect. This behaviour is consistent with that of styrene monomer in the trap system.[38] There is no response from the -100°C and -196°C traces throughout the temperature programme. This indicates that no non-condensable species are formed during degradation of the homopolymer.

At the end of the TVA experiments a yellow coloured'cold ring' fraction was observed at the top of the degradation tube. There was however, no residue remaining after heating to 500°C.

(b) Degradation Products

No detailed analysis of each fraction of degradation products was carried out, since they have been thoroughly examined by previous workers.[79,81] A brief qualitative study was made, however, on each degradation fraction using standard analytical methods. The condensable fraction was identified as styrene monomer with traces of toluene and benzene. The 'cold ring' fraction was found to consist of styrene type oligomers.

8.4 2BEM-S COPOLYMER

The polymerisation conditions employed in the preparation of

this copolymer have been described in Chapter 2. The reactivity ratios for the radical polymerisation at 60°C have already been determined by Luskin and Myers[35], who found r_1(2BEM) = 0.44 ± 0.02, r_2 (S) = 0.35 ± 0.02. These reactivity ratios were used to calculate the monomer feed ratio which would produce a 1:1 monomer ratio in the compolymer.

The copolymer composition was determined by the microanalysis method described in Chapter 3. Figure 8.2 shows the curve obtained when the theoretical monomer ratios in the copolymer are plotted against the corresponding percentage bromine values. Microanalysis indicated that the bromine content of the copolymer was 25.9wt%, which gives a monomer composition ratio of 52:48, S:2BEM.

The NMR spectroscopic method employed for analysis of 2BEM-MA copolymers was not applicable in this system as there was substantial overlap of the methine and methylene proton absorptions of the styrene group with the bromoethyl group proton absorptions of the methacrylate side chain as illustrated in Figure 8.3. This diagram also includes the 100MHz NMR spectrum obtained from PS homopolymer. The most obvious feature between the two resides in the aromatic proton absorption region 6.5 - 7.4 δ .

In the PS spectrum two distinct peaks are discernable at 7.05 δ and 6.54 δ , with an integral ratio of 3:2 respectively. Substitution experiments have shown that these peaks correspond to meta-para and ortho protons respectively.[87]

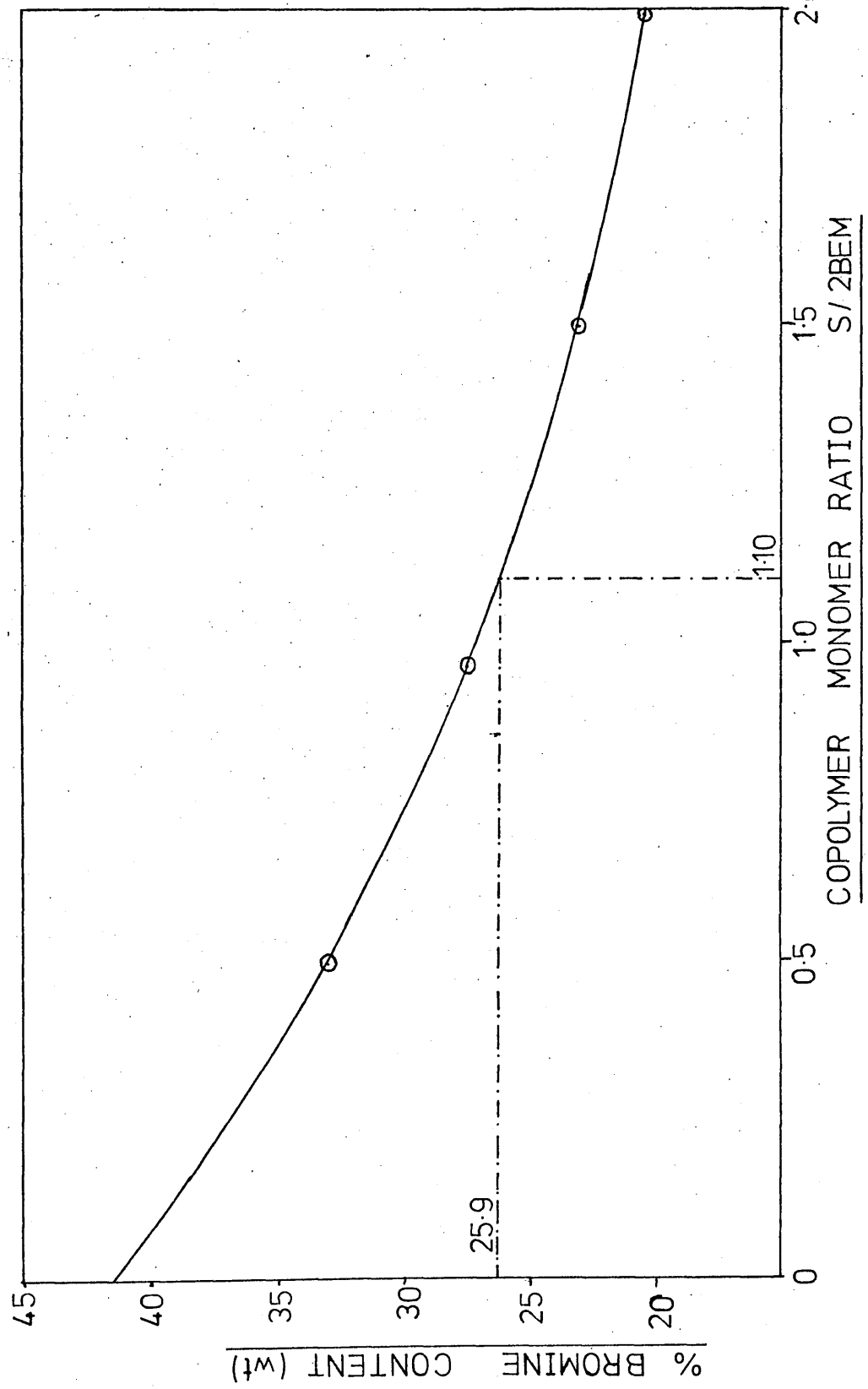


FIGURE 8.2 GRAPH OF % BROMINE CONTENT IN COPOLYMER vs THEORETICAL COPOLYMER MONOMER COMPOSITIONS.

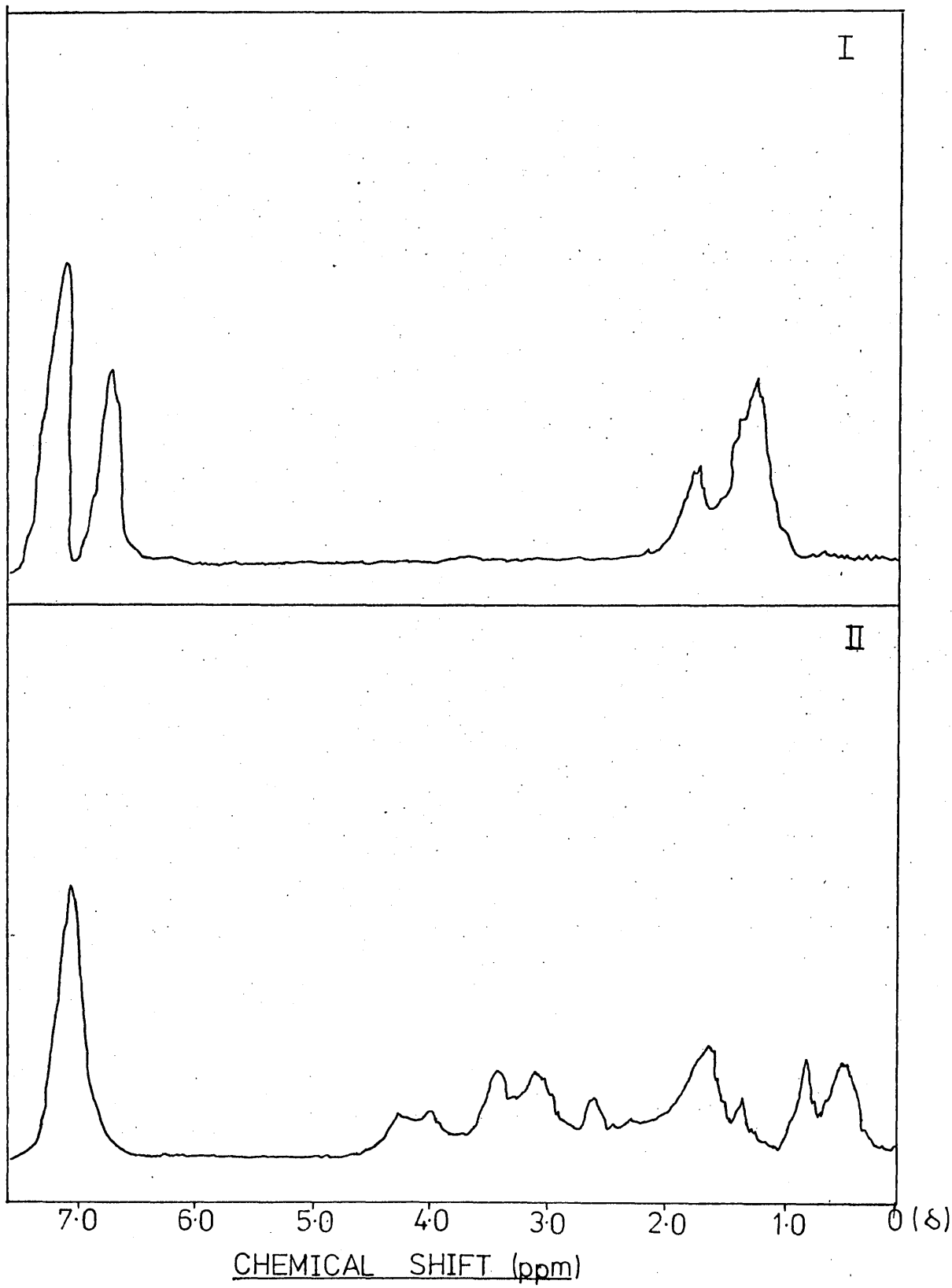


FIGURE 8.3 NMR SPECTRA OF (I) POLYSTYRENE (100 MH_2)

(II) COPOLYMER 2BEM/S (90 MH_2) ($CDCl_3$ SOLUTION)

The chemical shifts of these protons are lower than those in comparable small molecules; the meta-para protons being shifted upfield by 0.2 δ units and the ortho protons by 0.7 δ units. Bovey et al[88] have explained this shift in terms of intramolecular stacking of phenyl rings clustered together. This phenyl grouping has a greater effect on the ortho protons than on the other aromatic protons and has also been shown[88] to effect the α-substituent causing increased shielding of the methine proton by 1.1 δ units. These workers have also found that these anomalous effects are visually observable when styrene units occur in sequences of nine or more units. Mochel[89] has analysed the aromatic proton absorption profile by an Analog Computer method which can detect anomalous effects from two or three sequential styrene units.

These anomalous shifts can therefore be used to estimate the lengths of styrene block sequences in copolymers. In the present 2BEM-S copolymer system, as observed in Figure 8.3, only one peak is present in the aromatic proton absorption region of the NMR spectrum at 90MHz. There is however, a noticeable tail on this peak to lower δ chemical shift values. From sequence distribution data using Harwood's methods[73] and using the reactivity ratios found by Luskin and Myers[35] the fraction of styrene units which appear in the middle of styrene triads in the copolymer is 0.099. Thus, one in ten styrene units have an immediate environment comparable with PS homopolymer. The NMR spectrum of the copolymer shows only a slight broadening of the aromatic absorption region to a higher field value which concurs with sequence distribution data and confirms

that the copolymer is dominantly of an alternating nature. The NMR spectrum of copolymers containing styrene units can therefore give a quick qualitative guide to the sequence distribution and copolymer composition.

The copolymer 2BEM-S was found to be readily soluble in most of the common solvents such as acetone, toluene and chloroform. It was a white powder and had an average molecular weight of 109,000.

8.5 THERMAL ANALYSIS

(i) Thermogravimetry

The weight loss curve for 10 mgs of copolymer 2BEM-S is compared in Figure 8.4 with those for P2BEM and PS homopolymers. The copolymer shows a single stage reaction with complete volatilisation by 425°C. The weight loss begins at approximately 300°C and reaches a maximum rate at 367°C. The stability of the copolymer is intermediate between those of the homopolymers and shows no low temperature weight loss, which is present in the methacrylate homopolymer.

(ii) TVA

The thermogram obtained from a 50mg powdered sample of copolymer B is illustrated in Figure 8.5. A single main peak with Tmax at 370°C is clearly observable. However, a small plateau at temperatures in the region of 405°C is also apparent. Volatilisation of condensable species begins at approximately 280°C and continues right up to 500°C.

The separation of the various temperature traces suggests that a variety of condensables with a range of volatility is being

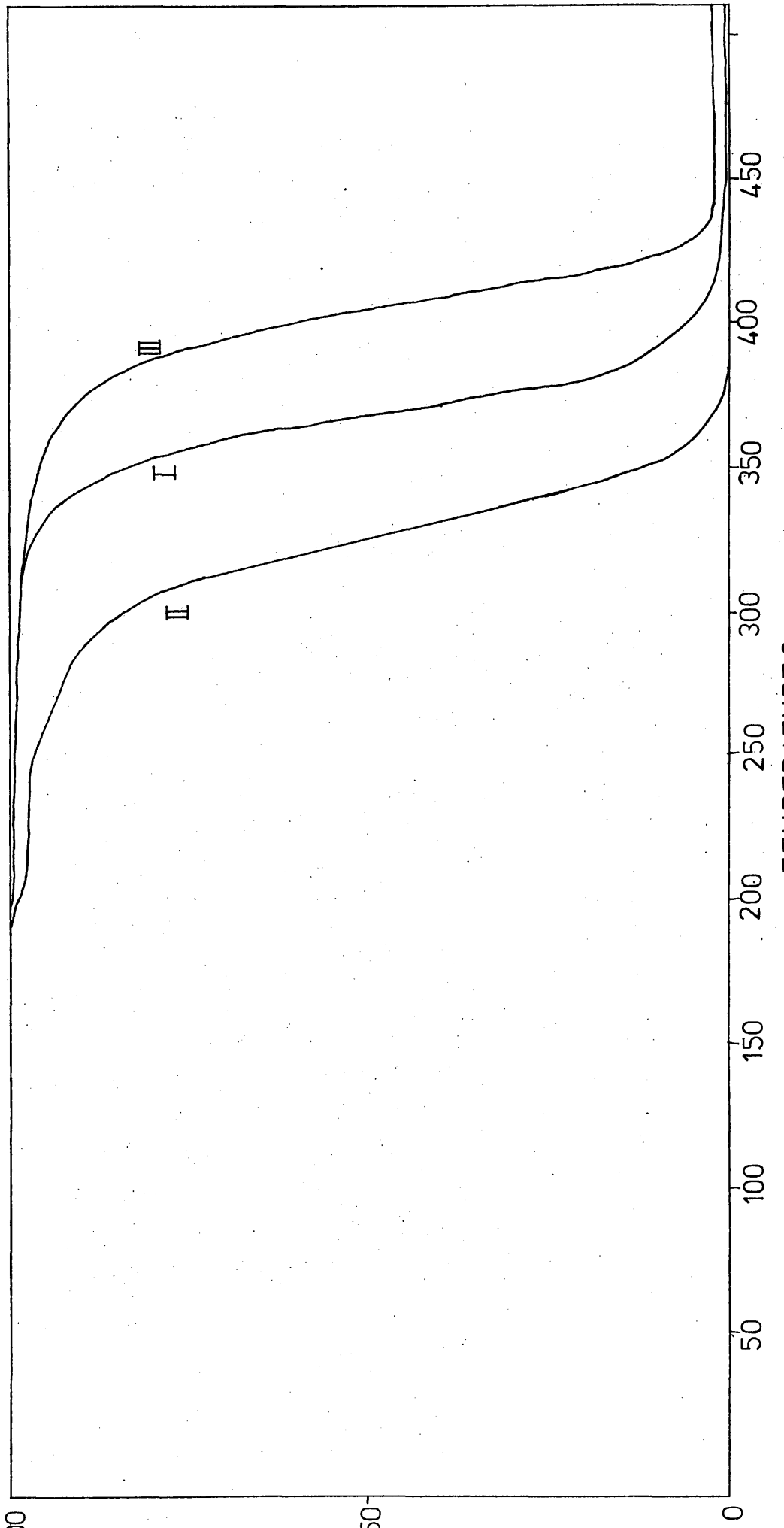


FIGURE 8.4 TG CURVE FOR (I) COPOLYMER 2BEM-S (10 mg) (II) P2BEM (III) PS.

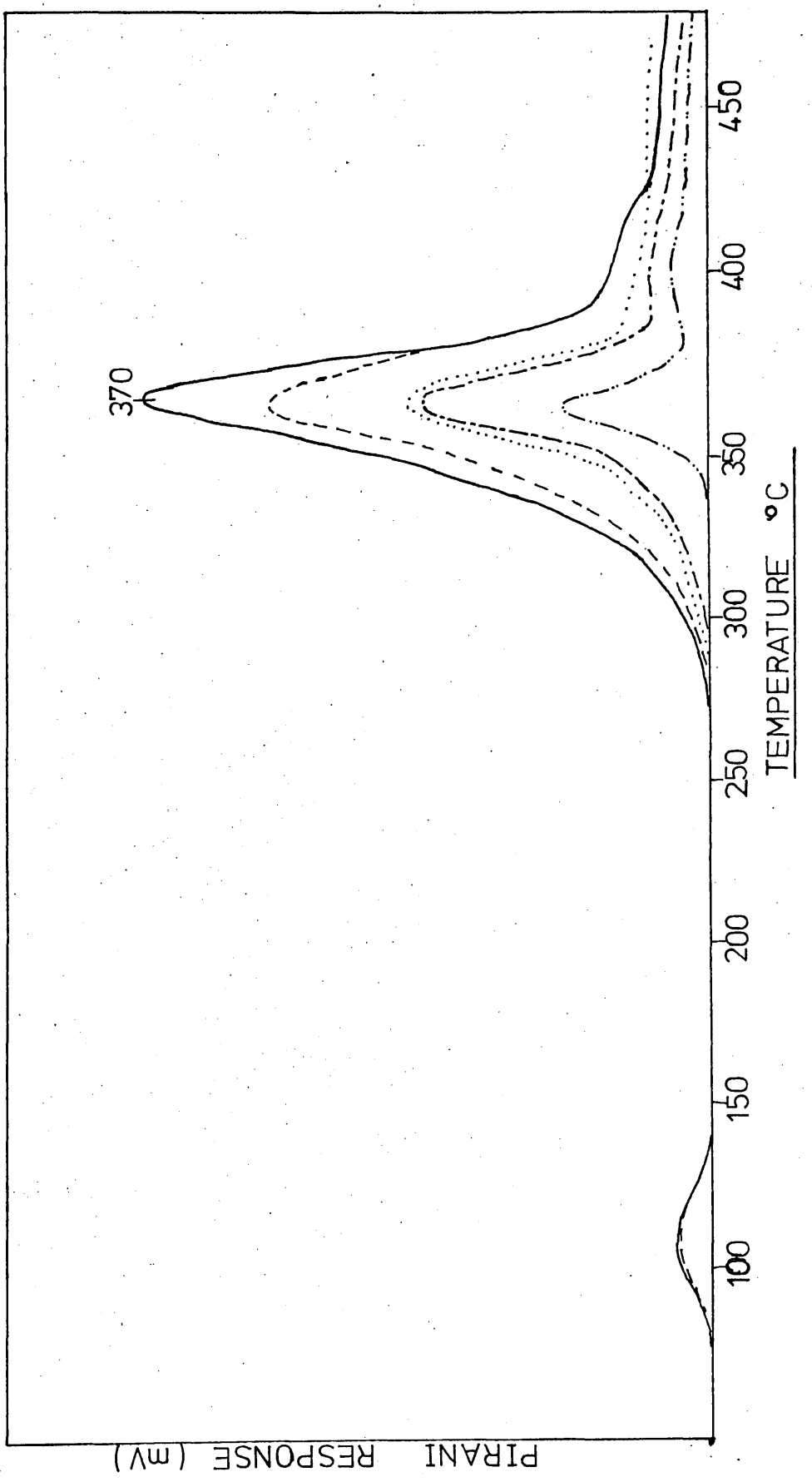


FIGURE 8.5 TVA TRACE OF COPOLYMER 2BEM/S (20 mg POWDER).

evolved from the copolymer system during the degradation reaction. The separation of the $0^{o}C$ and the $-45^{o}C$ traces for instance, is indicative of the production of 2BEM monomer or an equivalent high boiling product. The fairly large separation of the $-45^{o}C$ and $-75^{o}C$ traces also suggests the presence of styrene among the condensable volatile fraction.[38] This suggestion is further supported by the small limiting rate effect exhibited by the $-75^{o}C$ trace at higher temperatures. The $-75^{o}C$ and $-100^{o}C$ traces are virtually coincident throughout the main degradation stage but are separated from the $-196^{o}C$ trace. The response of these traces indicates the formation of small molecular volatile species during the main degradation reaction.

The response of the $-196^{o}C$ trace due to non-condensable species begins about $350^{o}C$ and follows the general volatilisation profile. It is noted that neither of the homopolymer systems yield non-condensable species during programmed heating to $500^{o}C$.

These condensable and non-condensable products account for about 70% of the original sample weight.

A yellow coloured'cold ring' fraction was observed after each degradation reaction and accounted for 28% of the original weight. It was examined in solution in carbon tetrachloride by infra-red and UV spectroscopy.

Virtually no residue remained after degradation to $500^{o}C$.

Comparison of the TVA data with that from thermogravimetry confirms that the weight-loss reaction corresponds to the evolution of material condensable at ambient temperatures.

It can also be concluded that the copolymer shows no low temperature volatilisation reaction comparable with that which occurs in P2BEM and that it has an intermediate stability with respect to the homopolymers. The various temperature traces of TVA also show that small volatile species including non-condensables which are not found among the degradation products of either hompolymer are being formed in the copolymer system.

This evidence suggests that substantial interaction between 2BEM and S units occurs in the degrading copolymer giving rise to a number of different products in addition to both monomers.

8.6 PRODUCT ANALYSIS

(i) Condensable Products

An essentially qualitative analysis of the degradation products from this copolymer system was undertaken using the standard analytical methods. A typical sub-ambient TVA trace of the condensable products from a programmed degradation to 500°C of 25mgs of copolymer B is shown in Figure 8.6. The products giving rise to the various peaks in the distillation system are presented in Table 8.1.

Table 8.1 Identification of Fractions in the Sub-ambient TVA Trace Illustrated in Figure 8.6

Peak	Products Identified
1	Ethylene
2	Carbon Dioxide
3	Hydrogen Bromide
4	Vinyl Bromide and Acetaldehyde (minor)
5	Styrene, Toluene (trace), Benzene (trace)
6	2-Bromoethyl Methacrylate

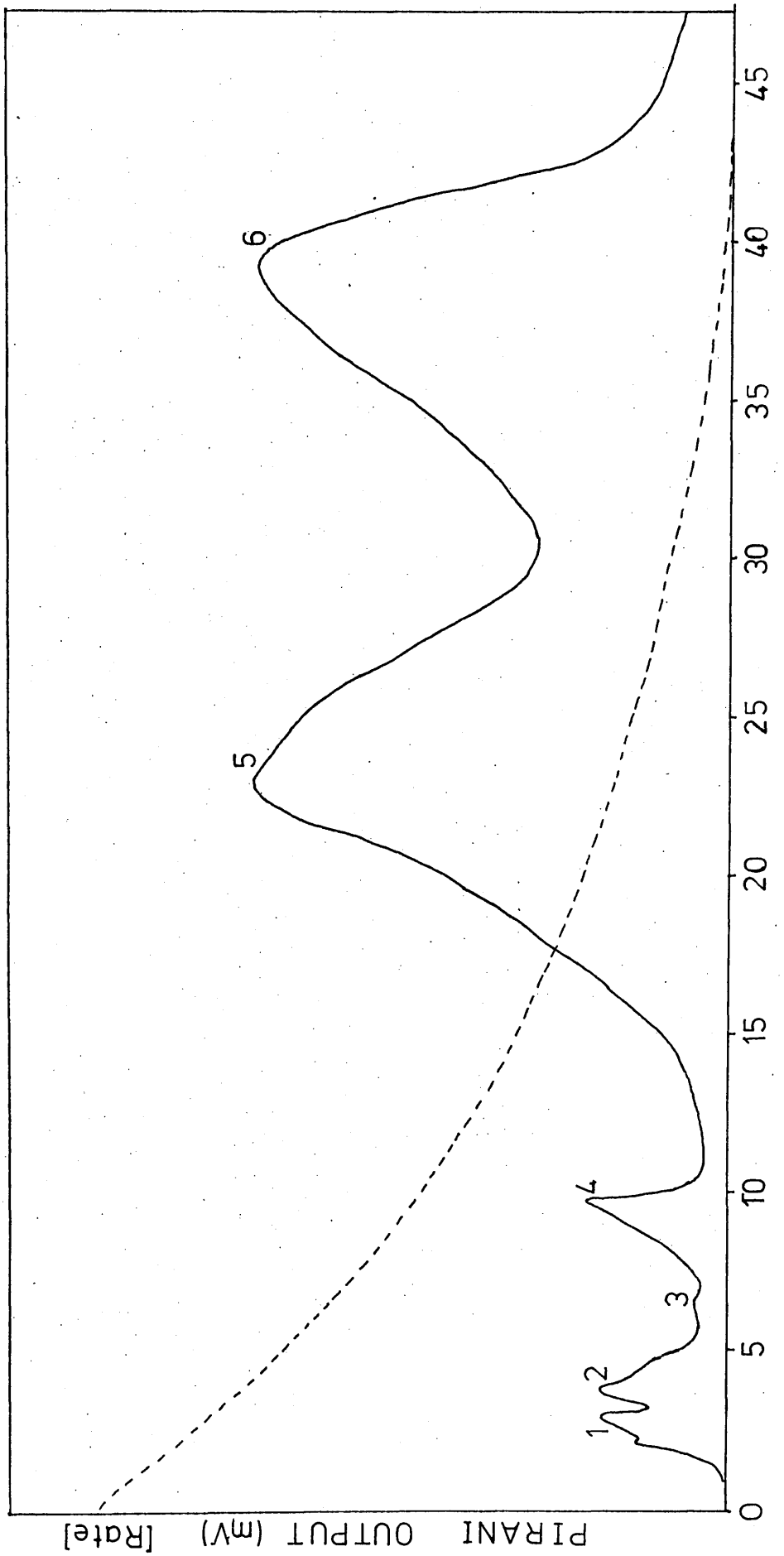


FIGURE 8.6 SUB-AMBIENT TVA TRACE OF 25 mgs COPOLYMER 2BEM-S DEGRADED TO 500°C AT 10°C/MIN.

Table 8.1 shows that in addition to the two monomers, ethylene, carbon dioxide, hydrogen bromide, vinyl bromide and acetaldehyde are also present among the condensable products of degradation. These findings confirm the information afforded by TVA, that an interaction between the two degrading monomer units certainly takes place in the degrading copolymer system to give volatiles not produced from either homopolymer. It would seem that carbon dioxide is produced in greater amounts than ethylene, although by far the main components of this fraction are the two monomers, styrene and 2BEM.

Hydrogen bromide and acetaldehyde are produced in minor amounts.

(ii) Non-Condensable Products

These were collected by heating 25 mgs of the copolymer in a sealed tube for one hour at 400°C and transferring the gaseous products to an infra-red gas cell by means of a Toeppler pump. Infra-red spectroscopy and mass spectrometry showed that methane was the chief non-condensable product with a small amount of carbon monoxide. No hydrogen was detected.

(iii) Cold Ring Fraction

UV and infra-red spectral analysis was carried out on carbon tetrachloride solutions of this coloured fraction. Figure 8.7 shows the UV spectrum in the region 250-400 nm of both the undegraded copolymer polystyrene, and the 'cold ring' fraction from degradation. The complex absorption profile of the undegraded sample changes to a broad absorption covering the whole spectral range in the 'cold ring' fraction. This complex absorption profile shown by the copolymer is the same as that shown by

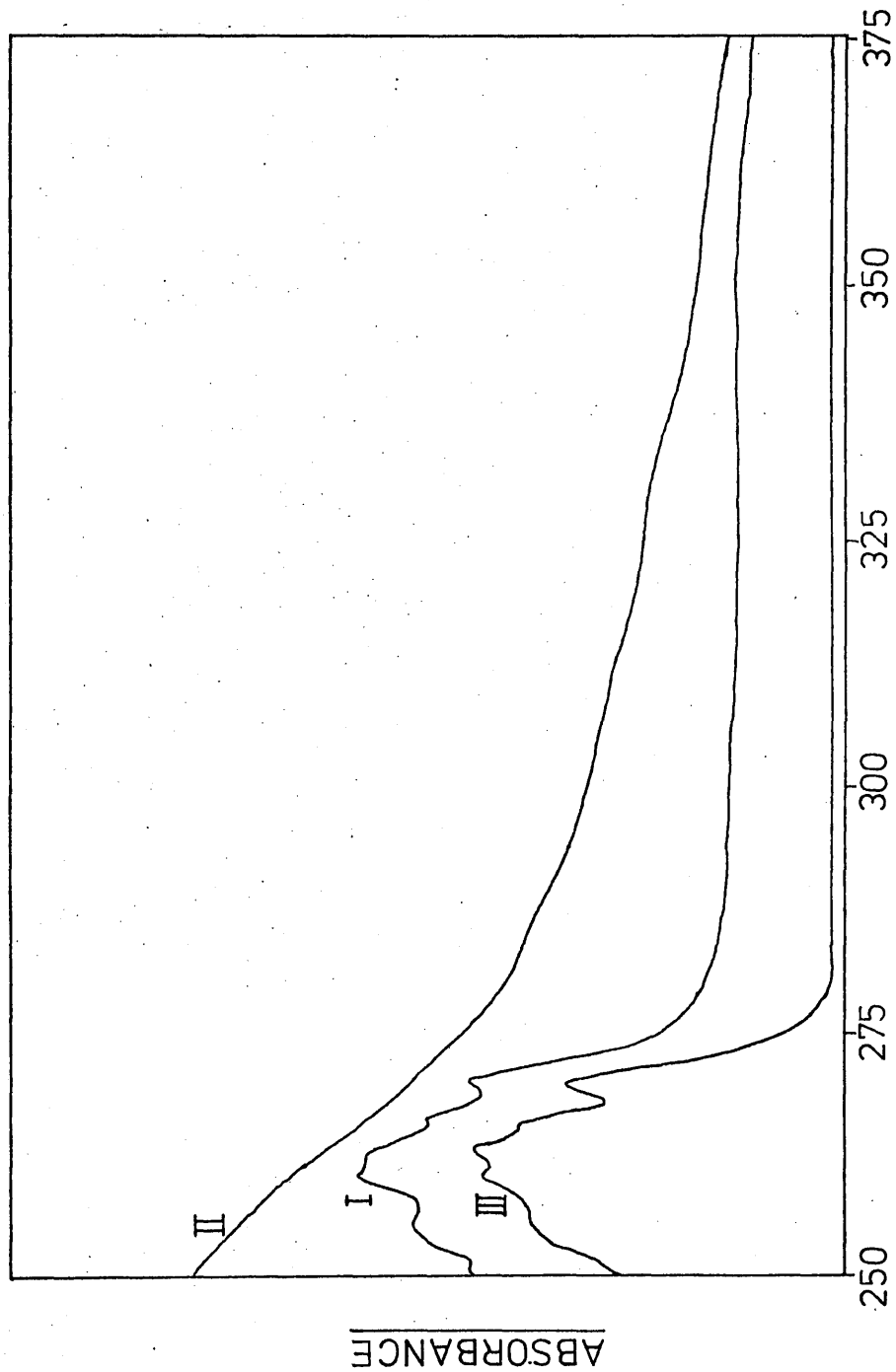


FIGURE 8.7 UV SPECTRA OF (I) UNDEGRADED COPOLYMER B (II) COLD RING FRACTION (III) POLYSTYRENE (CCl_4 SOLUTIONS).

polystyrene itself (Curve III in Figure 8.7) and corresponds to the forbidden transition band of benzene in the 2600 Å region as noted by Klevens.[90] This absorption in the copolymer is not influenced by the presence of the comonomer 2BEM. Curve II in Figure 8.7 shows no such fine structure in that region of the spectrum but does show a broadening of the absorption up to 350 nm. This broadening suggests the formation of conjugated structures in the polymer backbone which were also formed in the 'cold ring' fraction of 2BEM-MA copolymers. The spectral evidence suggests that the phenyl groups participate in this conjugation. Data presented in Table 5.3 suggests that conjugated sequences of up to six units in length are present in the coloured 'cold ring' fraction.

The infra-red spectrum of both the undegraded copolymer and the 'cold ring' fraction are shown in Figure 8.8. The spectrum of the 'cold ring' fraction differs from that of the original copolymer in a number of aspects:-

(a) The carbonyl region has developed two peaks at 1807cm^{-1} and 1767cm^{-1} which are indicative of a six membered anhydride ring structure. There is also evidence of a new peak at 1022cm^{-1} attributable to the C-O-C rocking vibration of such a structure. A shoulder at 1695cm^{-1} is also observable on the main carbonyl peak the relative intensity of which is reduced with respect to the peak at 700cm^{-1} attributed to a deformation mode of the styrene unit.

(b) A new absorption at 1630cm^{-1} confirms the existence of carbon-carbon double bonds which occur in conjugated sequences

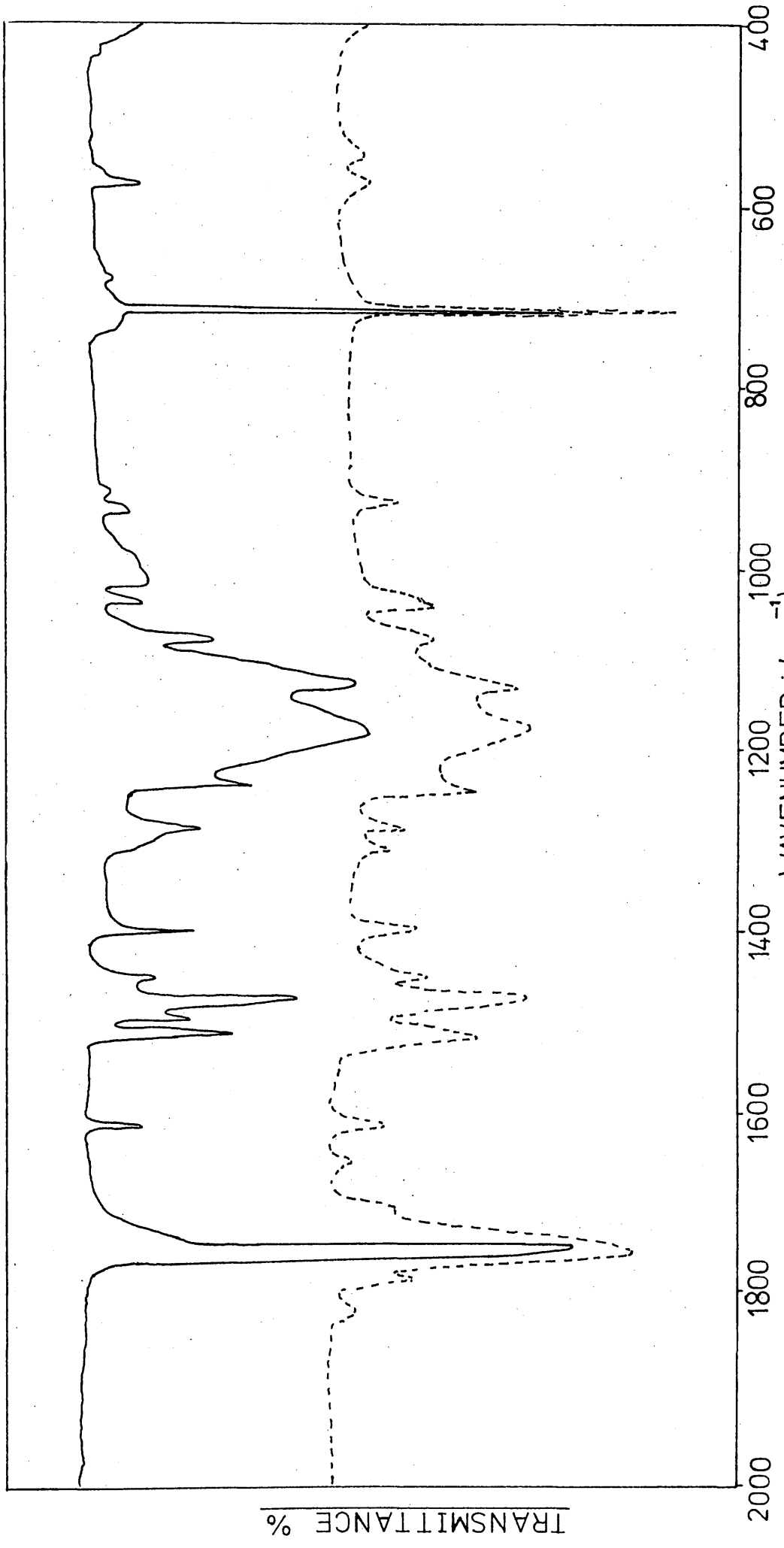


FIGURE 8.8 INFRA-RED SPECTRUM OF UNDEGRADED COPOLYMER (—), COLD RING FRACTION (---) (CCl_4 SOLUTION).

as suggested by UV spectroscopy.

(c) A number of peaks attributed to the 2BEM units are either not present, reduced in intensity, or are displaced in the spectrum of the involatile fraction. For example, the peak at 1417cm^{-1} in the undegraded sample which occurs in P2BEM is not present in spectrum II; the carbonyl carbon - oxygen stretching mode is shifted from 1182cm^{-1} in spectrum I to 1160cm^{-1} in the spectrum of the 'cold ring' fraction.

These observations suggest that the 'cold ring' fraction contains 2BEM units which are chemically modified compared with those in the undegraded polymer.

(d) Two weak absorptions at 579cm^{-1} and 550cm^{-1} are present in spectrum II compared to the one medium strength peak at 580cm^{-1} in spectrum I. The higher frequency absorption at 580cm^{-1} is due to a primary carbon-bromine stretching mode corresponding to the side group of the methacrylate monomer unit. This absorption however, has diminished in relative intensity in the spectrum of the 'cold ring' fraction. This suggests a decrease in the concentration of such carbon-bromine bonds in the degraded fraction. As this peak is reduced a corresponding new peak developes at 550cm^{-1}. Secondary carbon-bromine bonds normally absorb in the region 550-540cm^{-1}.[91] Hence, the occurrence of this new peak may be associated with the presence of secondary carbon-bromine bonds in this fraction.

All of this spectral evidence suggests that not only are 2BEM units present in the 'cold ring' fraction but that some proportion of them have undergone some intra-molecular cyclisation

reaction to form a 6-membered anhydride ring structure. There is also evidence from both UV and infra-red spectroscopy of the existence of sequences of conjugated carbon-carbon double bonds of up to six units in length. The pendant phenyl groups of the styrene units also seem to be part of this conjugated structure. The carbon-bromine stretching region indicates the formation of a secondary carbon-bromine bond with a corresponding decrease in the primary carbon-bromine absorption.

8.7 DISCUSSION

From the weight loss and volatilisation information it is evident that this 2BEM-S copolymer system has an intermediate stability with respect to the homopolymers. It is also apparent that this copolymer shows no low temperature instability which is present in P2BEM and attributed to depolymerisation initiated at unsaturated chain-end structures formed in the disproportional terminated step during polymerisation. Bevington, Melville and Taylor[71] have shown that in styrene/MMA copolymers, prepared under similar conditions to those in the present work, most of the termination occurs by a combination reaction of unlike radicals. Thus, by analogy, it would seem that the apparent stability of the 2BEM/S copolymer can be satisfactorily explained in terms of a reduction in the number of unsaturated 2BEM end groups which are present in the copolymer system. Grassie and Farish[72] reached the same conclusion following their work on the thermal degradation characteristics of copolymers of styrene and MMA. These workers also found that the degradation products from a series of copolymers of S/MMA consisted mainly of both monomers

and that sequences of at least ten styrene units were necessary for the production of styrene dimer, trimer and tetramer. In agreement with Wall[92] they also determined that none of the degradation products larger than monomer contained MMA units. Grassie and Farish[72] also found that only 3% of the styrene units were evolved as non-monomer products from a 1:1 S:MMA copolymer composition.

As observed in Chapter 4, the thermal degradation behaviour of P2BEM is analogous to that of PMMA, with an almost exclusive depolymerisation reaction producing 2BFM monomer. It would be expected therefore, that 2BEM/S copolymers should display a similar breakdown behaviour to that of MMA/S copolymers, as studied by Grassie and Farish.[72] Although both monomers are the principal degradation products from both copolymer systems, the 2BEM/S copolymer decomposition displays a number of additional features:-

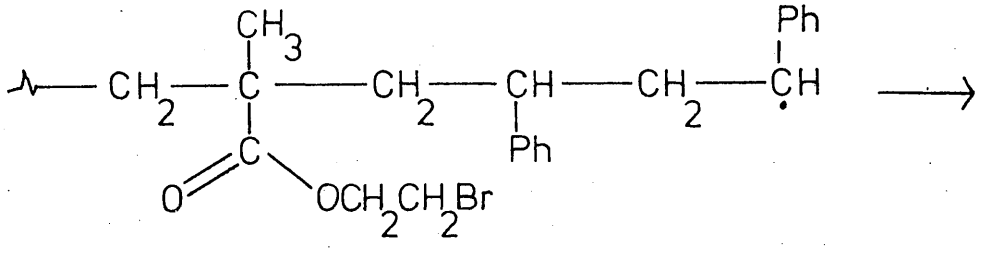
(i) Volatiles other than the two monomers are produced during the main decomposition reaction. These include non-condensable species which are absent from the degradation products of the homopolymers. The nature and amounts of these volatiles suggest that an interaction takes place between degrading styrene and 2BEM units in competition with straightforward depropagation, although to a much smaller extent.

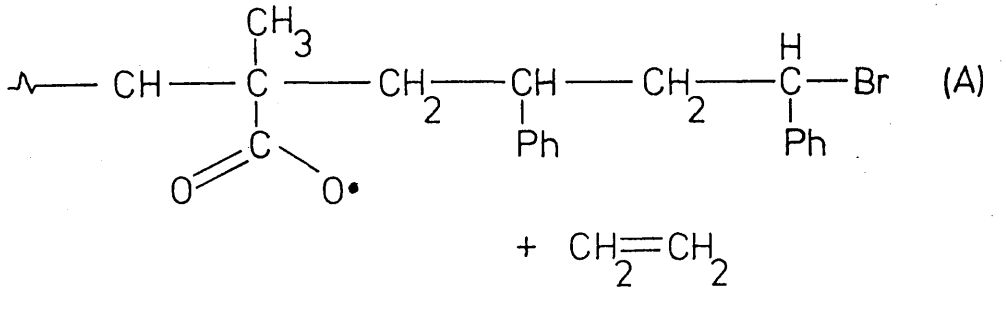
(ii) A larger proportion of 'cold ring' fraction is formed in the degradation of the 2BEM-S copolymer compared with a similar copolymer composition in the MMA/S system. This, in addition to

the fact that 2BEM groups and modified 2BEM structures are present in this fraction suggests that it may consist of modified chain fragments, and not styrene oligomers. There is also evidence that the phenyl groups on the styrene units participate in conjugation along the main chain backbone, giving rise to colour.

The only essential difference between 2BEM and MMA units is the presence of the bromine atom on the ester side chain. This anomalous behaviour may, therefore, be best resolved by considering the effects which degrading styrene radicals may have on this particular brominated group.

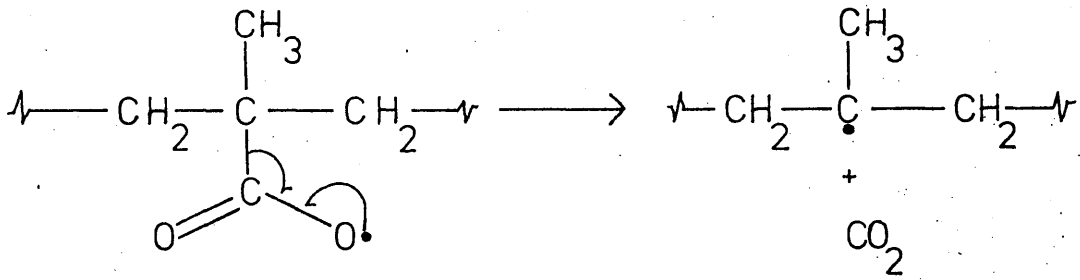
It has been established that transfer processes are an integral part of the mechanism of degradation in polystyrenes.[79,81] The formation of the oligomer fraction is due to intramolecular transfer of a tertiary hydrogen atom to a chain terminal radical followed by chain scission. Although the 2BEM unit does not incorporate a tertiary hydrogen atom, abstraction of a bromine atom by the relatively stabilised styrene terminal radical is an alternative reaction. This reaction may occur intra-or intermolecularly although the former process is favoured in polystyrene itself. The following reaction sequence is proposed to explain the formation of ethylene, incorporating the bromine transfer step:-



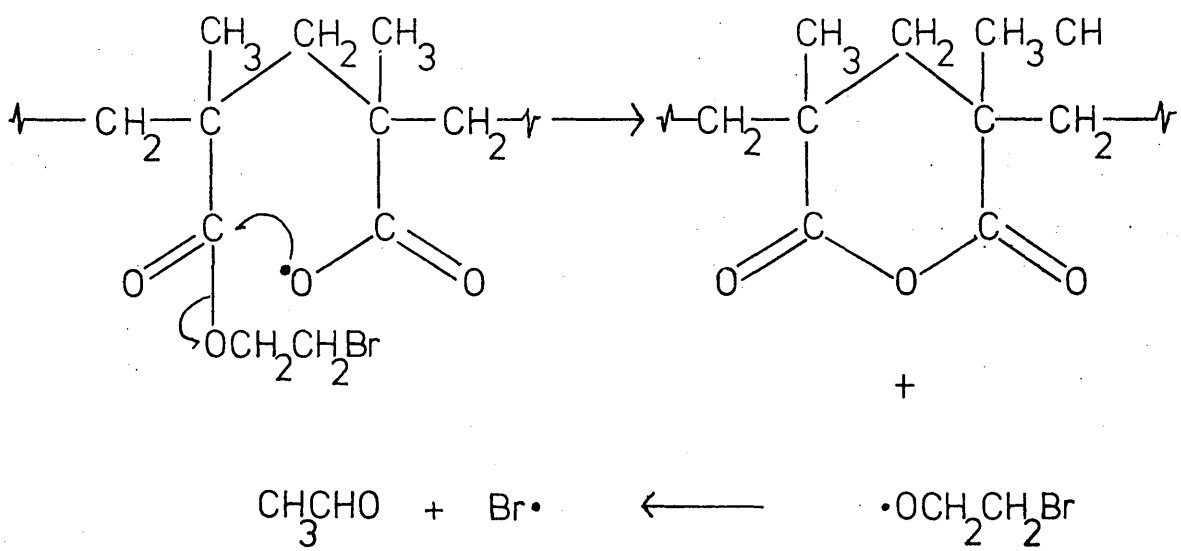


(A)

The carboxy radical A which remains after ethylene formation may react in two ways; it may either decarboxylate to generate carbon dioxide and a polymer radical,



or it may undergo a cyclisation reaction with a neighbouring 2BEM unit to give a six-membered anhydride ring structure and a brominated ethoxy radical which can rearrange itself to give acetaldehyde and a free bromine atom:-



Hence, these series of reactions initiated by bromine atom transfer may explain the formation of not only ethylene, acetal-

dehyde and carbon dioxide but also the presence of anhydride structures in the 'cold ring' fraction.

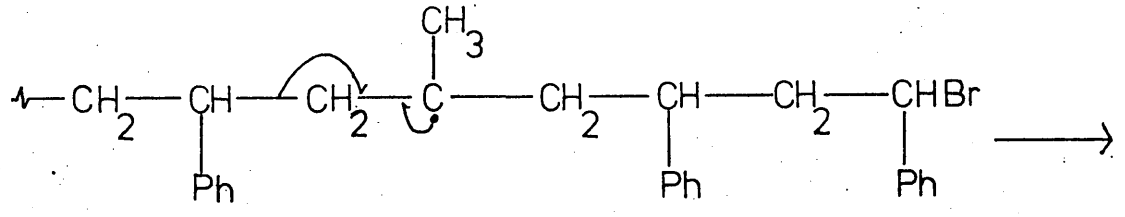
The bromine atoms which are released during the rearrangement of the ethoxy radical can then abstract a proton, probably a tertiary hydrogen atom on a styrene unit, to form hydrogen bromide. The production of acetaldehyde from the brominated ethoxy radical has been previously established in Chapter 4.

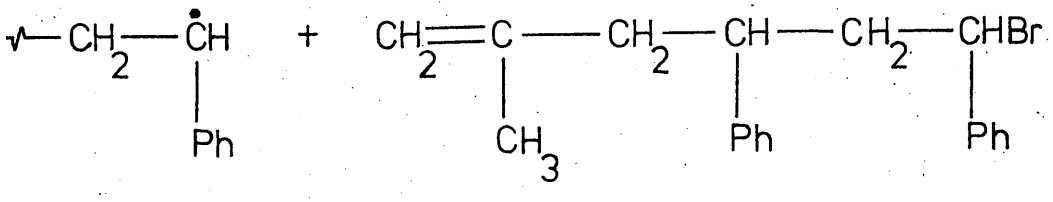
The presence of ethylene among the degradation products is evidence itself for the bromine transfer mechanism because it is difficult to explain its formation by any other route. However, more direct evidence for this reaction lies in the infra-red spectrum of the 'cold ring' fraction. As discussed previously, the absorption band appearing at 550cm^{-1} is thought to be due to a secondary carbon-bromine bond stretching mode. This would correspond to the secondary carbon-bromine bond formed after bromine abstraction by a terminal styrene radical.

Although this halogen abstraction reaction is unusual in the thermal decomposition of polymers, Hrabák[93] and his co-workers have recently used this reaction to explain some degradation products of copolymers of styrene and 1,2,2,2-tetrachloroethyl esters of methacrylic and acrylic acid. These workers detected products such as benzyl chloride and 2-chloroethyl styrene by GCMS analysis from the flash pyrolysis of 0.5mg samples of the styrene/methacrylate copolymers heated to 310^{o}C. Hrabák et al[93] proposed that chlorine atoms attached to the methacrylate ester group were abstracted by degrading polystyrene chain radicals

to give halogenated styrene units which later decompose to give the observed products.

It is not clear whether in this present system this halogen abstraction reaction occurs by an intra-or intermolecular process. If it occurs intramolecularly and is followed by loss of ethylene and decarboxylation the remaining chain radical may undergo chain scission to give a small volatile chain fragment, which would condense on the upper part of the degradation tube, and a primary chain radical which may undergo depropagation.





An alternative chain scission reaction could yeild an unsaturated chain-end and a small vapourisable radical.

If the reaction occurred intermolecularly with subsequent evolution of ethylene and carbon dioxide, chain scission of the

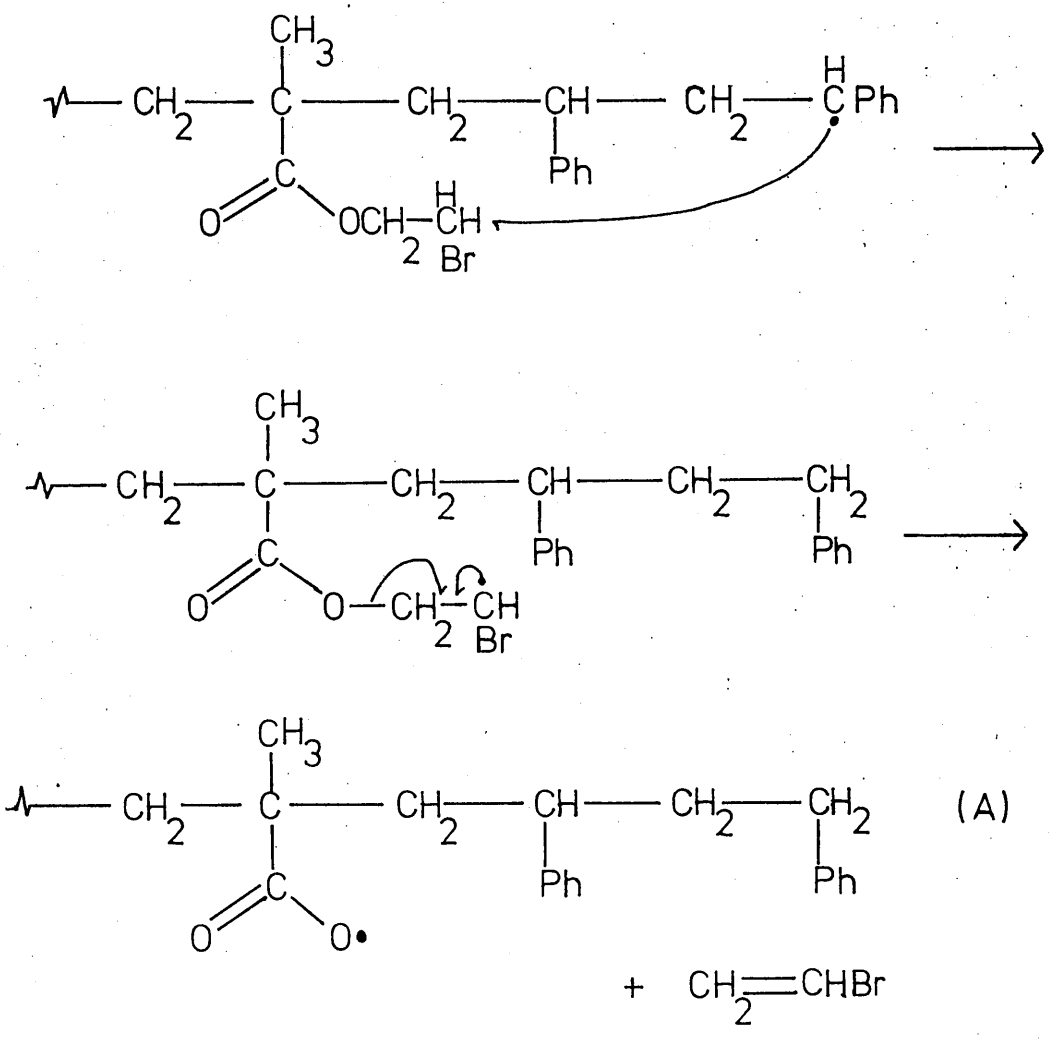
remaining polymer chain radical need not necessarily lead to volatilisation of a chain fragment. The fact that chain fragments constitute about 30% of the original weight suggests that the intramolecular process may predominate although some contribution from the intermolecular process cannot be entirely ruled out. In order to determine whether this intermolecular reaction does occur, a 1:1 by weight blend of PS/P2BEM was degraded at a programmed heating rate of $10^{o}C$/min. It was found that the P2BEM had completely volatilised before the PS homopolymer had begun to break down. No interaction was therefore observed. This result is in agreement with those of Grassie, McNeill and Cooke[94] who found no interaction between degrading mixtures of PMMA and PS.

In the copolymer, however, 2BEM units are present during the decomposition of the styrene groups and so an intermolecular process may be possible.

Vinyl Bromide Production

This product is formed in very small quantities during the degradation of P2BEM in an ester decomposition reaction. This reaction assumes greater importance however, whenever 2BEM units are exposed to temperatures greater than those at which depolymerisation normally takes place. This elimination can give rise to methacrylic acid units if it occurs by a molecular process, although this has normally been found to take place at lower temperatures.[17] It would appear however, that vinyl bromide is produced concurrently with the rest of the condensable volatiles in this copolymer system and may be associated with the main

degradation mechanism. It could well be formed in a competing hydrogen abstraction reaction involving a styrene polymer radical and a hydrogen on the ester side group of the methacrylate unit:-

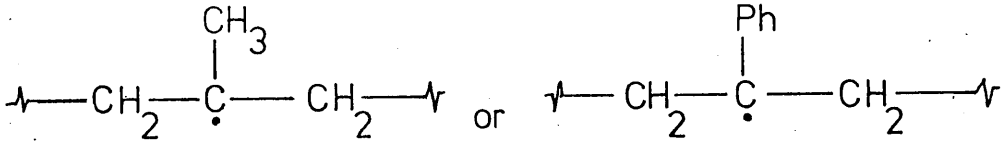


Although this is a secondary hydrogen atom it is attached to a carbon which carries a bromine atom. The electronegativity of the bromine atom will decrease the strength of the carbon-hydrogen bond and make the proton more readily available for abstraction. This reaction also gives rise to the carboxy radical A which may

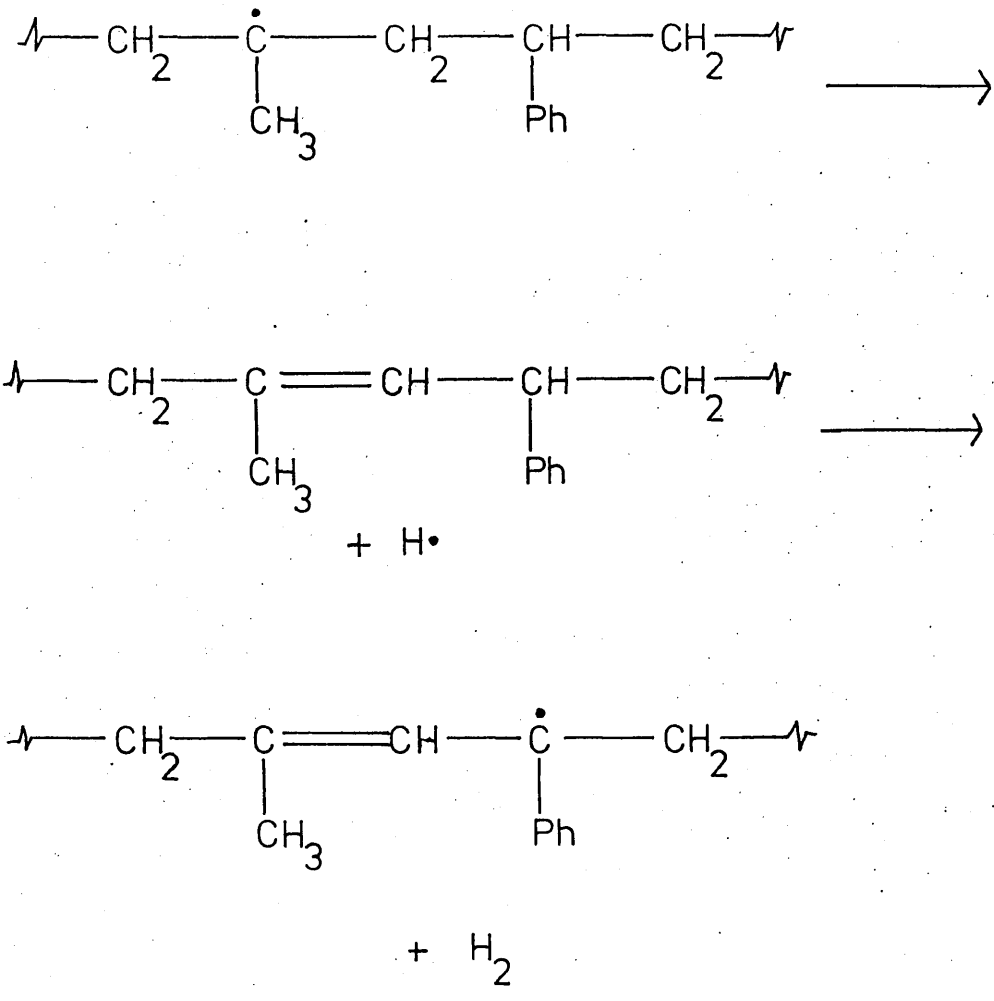
decompose by the routes previously discussed, giving rise to carbon dioxide, acetaldehyde and six-membered anhydride ring structures. It could also result in the formation of hydrogen bromide by reaction of the free bromine atom relased by acetaldehyde production.

It appears therefore, that this hydrogen abstraction process occurs in competition with bromine transfer, the former process giving rise to vinyl bromide and the latter to ethylene. The relative likelihood of these two processes taking place will be reflected in the quantitative production of the two volatile products. Information from sub-ambient TVA suggests that both transfer steps have a roughly equal probability.

The production of non-condensable species is thought to be associated with the development of colour, which has been shown to be due to sequences of unsaturated carbon-carbon double bonds. This conjugation was explained in terms of the loss of species such as hydrogen and methane from the polymer backbone in copolymers of 2BEM/MA. A similar reaction is thought to take place in the 2BEM/S system originating from radicals on the polymer backbone. These chain radicals are formed by either decarboxylation of the 2BEM unit or by hydrogen abstraction at a styrene unit, and may proceed



by a reaction which is an alternative to chain scission.



Monomer Production

The predominance of the two monomers indicates that the major decomposition reaction is depolymerisation. The importance of this reaction is not surprising considering that P2BEM breaks down almost exclusively to monomer while styrene accounts for 42% of the original PS homopolymer. Grassie and Farish[72] have shown that whenever styrene units are isolated in PMMA chains the unzipping reaction predominates. This is also the case in the 2BEM/S copolymer system although it does not occur to the complete exclusion of other processes. The initiation process

which gives rise to the primary radicals may originate at chain-end structures or by random chain scission.

Infra-red spectroscopy identified the presence of anhydride structures in the 'cold ring' fraction, although the concentration of such structures seemed rather low. These anhydride cyclic structures are known to decopose at temperatures greater than 400°C to give carbon dioxide, carbon monoxide and methane.[95] The small volatilisation peak observed over 400°C in the TVA of the copolymer may therefore be due to the decomposition of the anhydride rings which are formed in the acetaldehyde formation reaction.

Conclusions

All the features of the thermal degradation behaviour of 2BEM/S copolymers can be most satisfactorily accounted for in terms of an essentially free radical depolymerisation reaction with competing free radical halogen and hydrogen transfer steps. These transfer reactions are thought to occur in predominantly intramolecular processes with roughly equal probabilities and ultimately lead to a number of secondary reactions which include decarboxylation, chain scission, elimination and anhydride ring formation. The absence of unsaturated chain-end structures in the copolymer leads to increased thermal stability with respect to P2BEM homopolymer.

CHAPTER 9

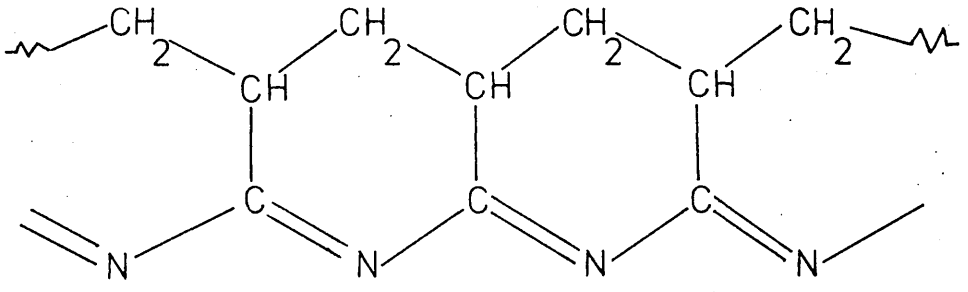
THERMAL DEGRADATION OF A 1:1 COPOLYMER OF 2-BROMOETHYL METHACRYLATE AND ACRYLONITRILE

9.1 INTRODUCTION

The work described in this chapter is concerned with the thermal degradation behaviour of an approximately 1:1 copolymer of 2BEM and acrylonitrile. Although this particular system has not previously been studied, there have been a number of publications dealing with the decomposition characteristics of related copolymer systems.[96,97] In particular, Grassie and McGuchan[96] have carried out a detailed investigation of the MMA/AN system employing the same thermal analytical techniques as those in the present study. Thus, the results from the 2BEM/AN copolymer will be discussed in relation to the findings of Grassie and McGuchan.[96] This chapter also includes an account of the principal features of the thermal breakdown of polyacrylonitrile (PAN) homopolymer.

9.2 THE THERMAL DECOMPOSITION OF POLYACRYLONITRILE

Whenever pure PAN is heated through a linear temperature programme in vacuum or in an inert atmosphere, a rapid exothermic reaction takes place at approximately 265°C accompanied by the evolution of gaseous products and the extensive formation of molecular chain fragments. The degrading polymer also discolours at temperatures in excess of 150°C. Various suggestions have been made about the chemical structure of the chromophore responsible for this discolouration[98,99,100,101] but it is now generally agreed that it is a conjugated polyimine[102,103,104]

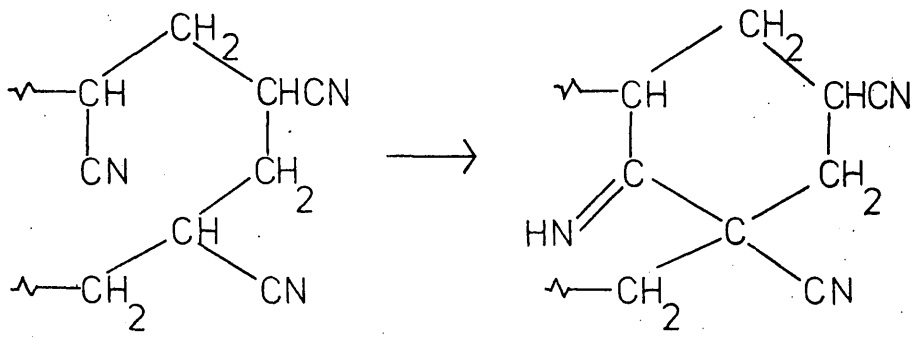


formed by cyclisation of the pendant nitrile groups.

On the basis of the nature of the volatiles evolved during the exothermic reaction and the extent of the accompanying weight loss Grassie and McGuchan[105,106] proposed that the zip length of this nitrile polymerisation is fairly short although the kinetic chain length of the overall process is long, being maintained by radical transfer reactions.[107] It has been estimated that 80% of the nitrile groups participate in the oligomerisation process.[108]

Grassie and Hay[104] suggested that the acidity of the methine

groups in PAN is sufficient to allow self-initiation of the cyclisation reaction which may also be intermolecular.



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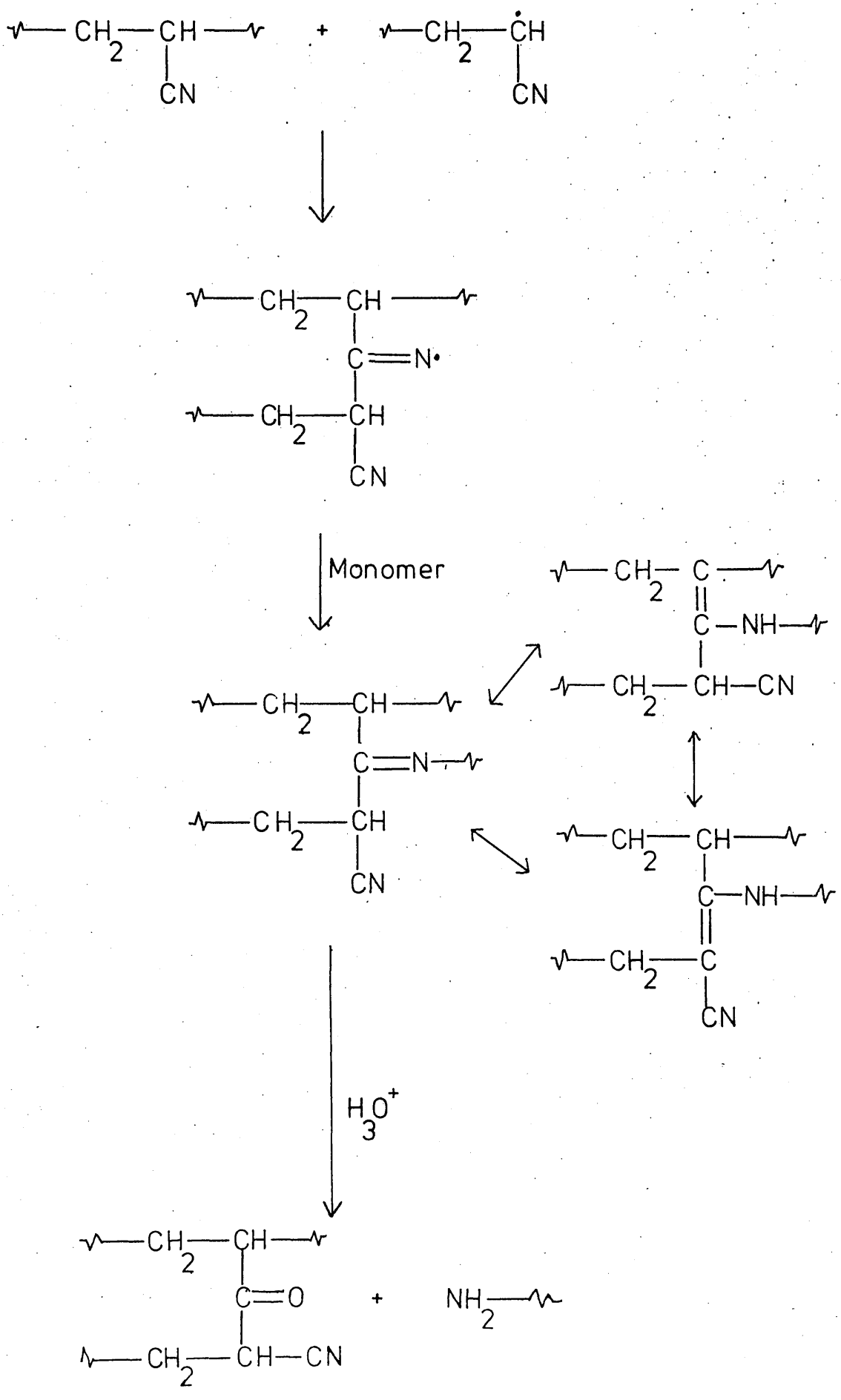
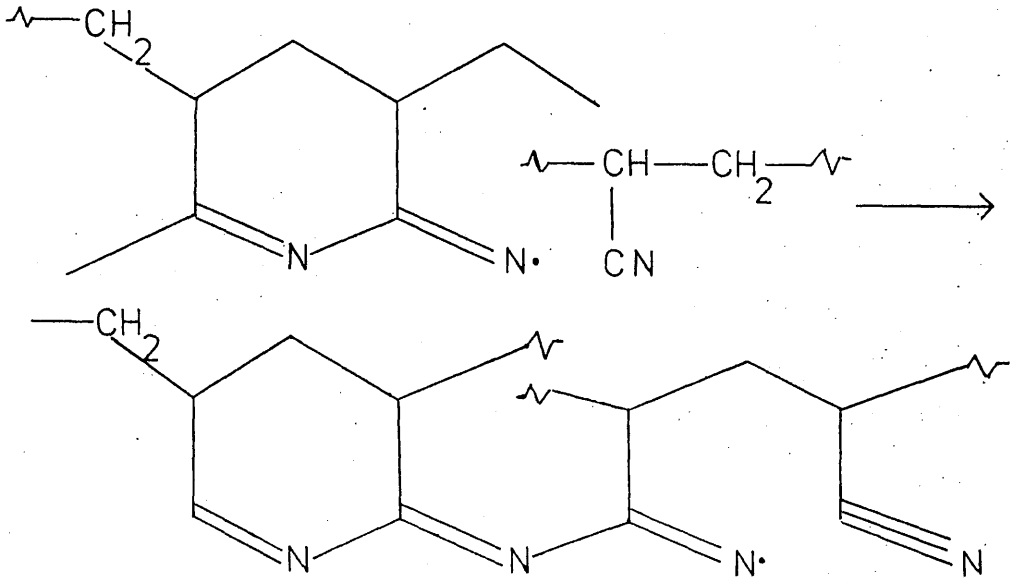
Peebles and his colleagues on the other hand, concluded that the reaction is initiated by abnormal structures distributed at random in the polymer molecules and which result from a side reaction during free radical polymerisation. According to Peebles[109] then, all free radical initiated PAN samples will incorporate either enamine structures, or if polymerisation conditions favour hydrolysis, ketonitrile structures.

In order to resolve this problem Grassie and McGuchan[106] studied the degradation behaviour of a variety of PAN homopolymers prepared using ionic and radical catalysts. They concluded that their results for radically prepared bulk polymers could be best explained in terms of initiation occurring at ketenamine abnormalities distributed throughout the polymer and that ketonitrile structures are slightly more stable with respect to initiating radical activity. Peebles[109] has also shown that the concentration of these abnormalities is dependent on the degree of conversion and mode of polymerisation.

The insolubility which develops in PAN during heating at


Monomer
H_3O^+
NH2

temperatures in excess of 150°C is thought to be due to an intermolecular reaction between pendant nitrile groups.[104]



In a series of papers by Grassie and McGuchan[105,106,109] the exothermic reaction and initial weight loss of pure PAN was studied by DTA, DSC, TGA and TVA. These workers found that the intensity and position of the endotherm was a function of heating rate, sample form and the amount of sample degraded, but that it occurred just before weight loss had begun. This means that considerable fragmentation of the polymer molecules must occur as a direct result of the exothermic phase of the reaction, especially at high heating rates, and the fragments are volatile enough to be removed from the sample at the reaction temperature and especially under vacuum.

Hydrogen cyanide and ammonia[105,110,111] are the principal products volatile at ordinary temperatures which are evolved during the initial sharp peak in the TVA profile which is shown in Figure 9.1. Some workers[112,113] have not detected ammonia among the products

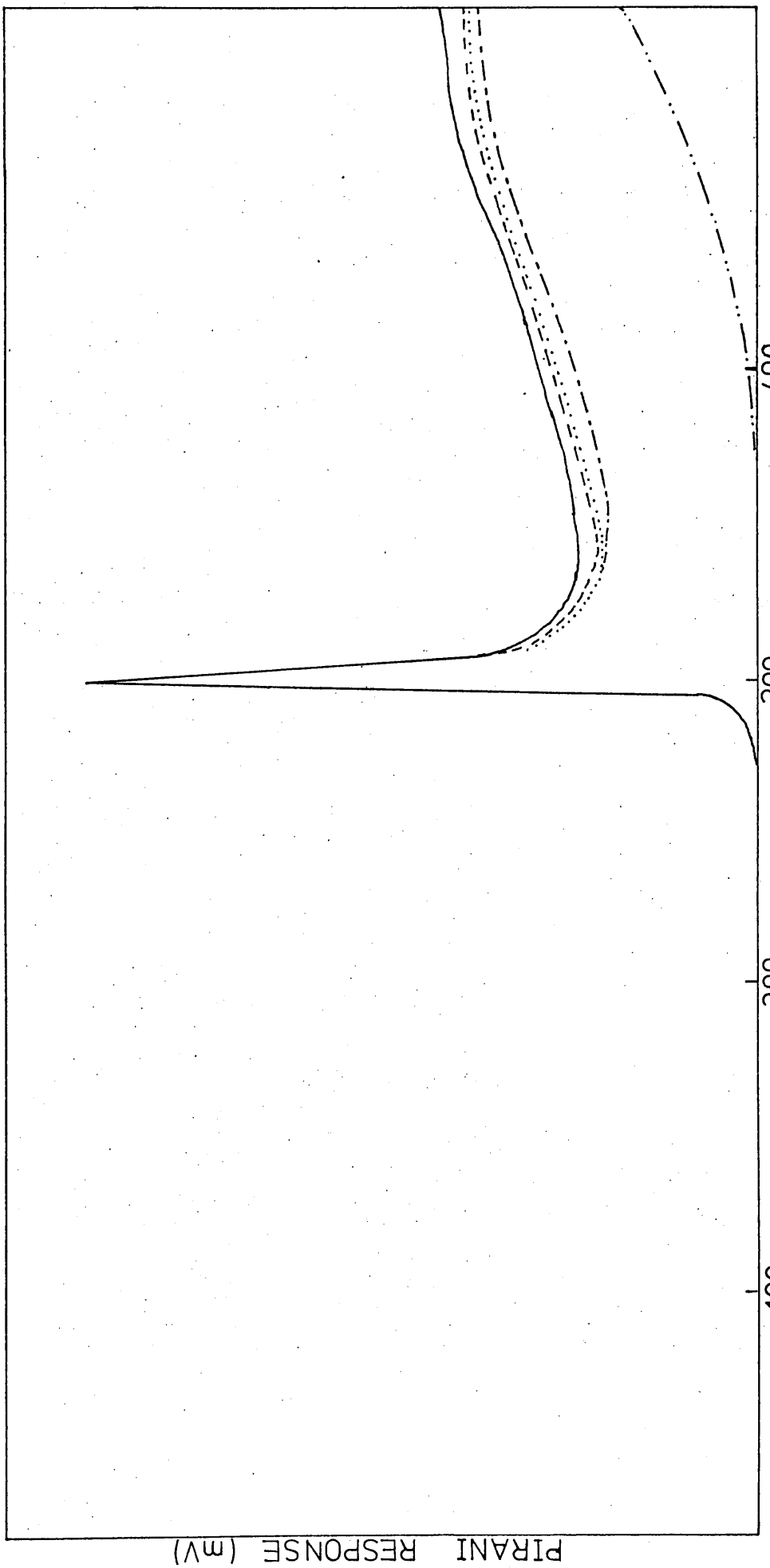


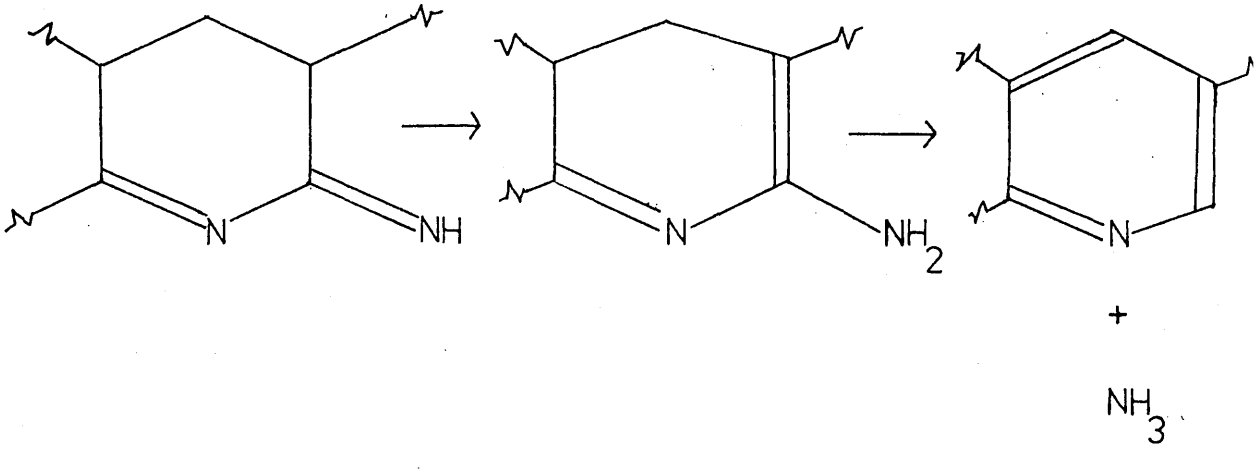
Figure 9.1 TVA of 80 mg of PAN degraded to 500°C at 10°C/min.

of degradation but more recently it has been established as a true decomposition product.

The TVA curve also shows a plateau in the region of 300-450°C which is again attributed to hydrogen cyanide and ammonia evolution. Non-condensable products identified as predominantly hydrogen with a trace of methane begin to be given off at temperatures above 350°C. The sensitivity of the Pirani gauge to hydrogen gas exaggerates the relative amount of non-condensable material present. A number of minor degradation products have been reported to be evolved above 300°C.[111,112,113] These include monomer, methacrylonitrile, cyanogen, vinylacetonitrile, acetonitrile and a number of aromatic nitriles.[114]

To reconcile the nature and distribution of these products and other features of the thermal decomposition described above, Grassie has recently proposed the following overall radical reaction sequence.[115]

The condensed nitrile sequences are thought to be fairly short, although the reaction is maintained kinetically by radical transfer processes. This produces a polymer chain consisting of short cyclised segments linked by segments of unchanged monomer units. Scission can occur at these latter structures to produce the 'cold ring' fraction with concurrent elimination of hydrogen cyanide from unchanged acrylonitrile units and ammonia derived from terminal imine groups:-[116]

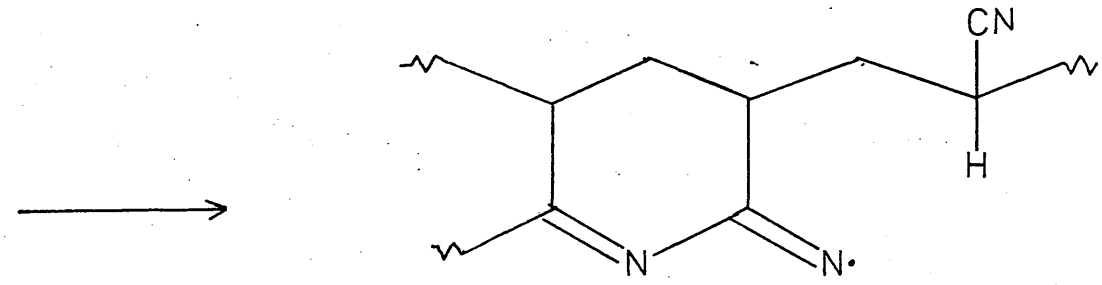


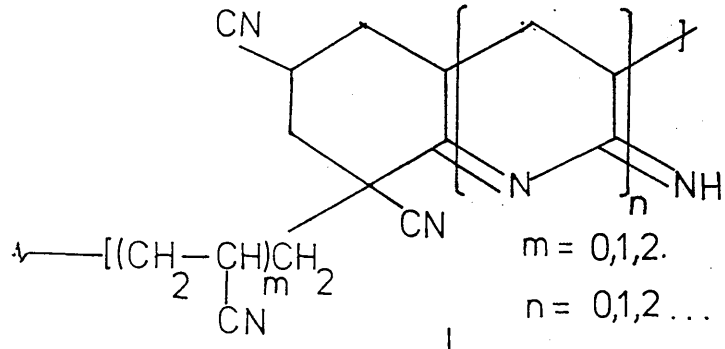
INITIATION

Abnormal structures

End structures

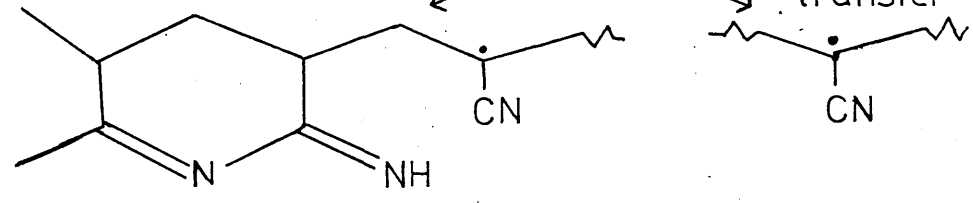
Impurities





H· abstraction

intra/intermolecular transfer



1. cyclisation
2. transfer

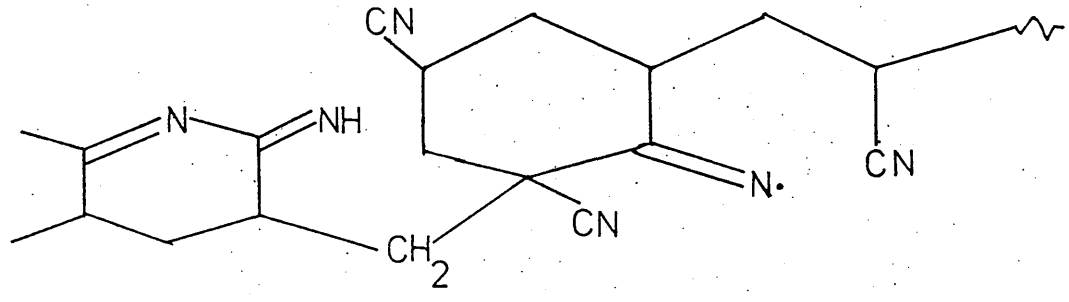
re-initiation

elimination & end group reactions

HCN, NH_3

chain scission

FRAGMENTS



At higher temperatures chain scission reactions allow the splitting out of trapped nitrile residues in the polymer chain while aromatisation of the cyclic imine structures leads to the production of hydrogen.

The ionically prepared polymers which have relatively less intense and much broader exotherms do not incorporate the enamine or ketonitrile groups present in radical polymers but it has been suggested that ionic species retained in these polymers may initiate cyclisation by an ionic mechanism.

9.3 2BEM/AN COPOLYMER

This copolymer was prepared and purified by the general method outlined in Chapter 2. No reactivity ratios for this monomer pair were available in the literature. However, Askarov and his co-workers[117] have studied the radical copolymerisation of 2-chloroethyl methacrylate (2CEM) and acrylonitrile (AN) at 60°C using a peroxide initiator and found r_1(AN) = 0.14 ± 0.02, r_2(2CEM) = 1.3 ± 0.2. These reactivity ratio values were used to calculate the monomer feed ratio required to produce a roughly 1:1 monomer ratio in the copolymer. The actual copolymer composition was determined by the microanalysis method described in Chapter 3, Figure 9.2 illustrates the curve obtained when the theoretical monomer ratios in the copolymer are plotted against the corresponding percentage bromine values. Microanalysis indicated that the bromine content of the copolymer was 32.9% which corresponds to a monomer composition ratio of 49/51, AN/2BEM. This result suggests that the reactivity ratios

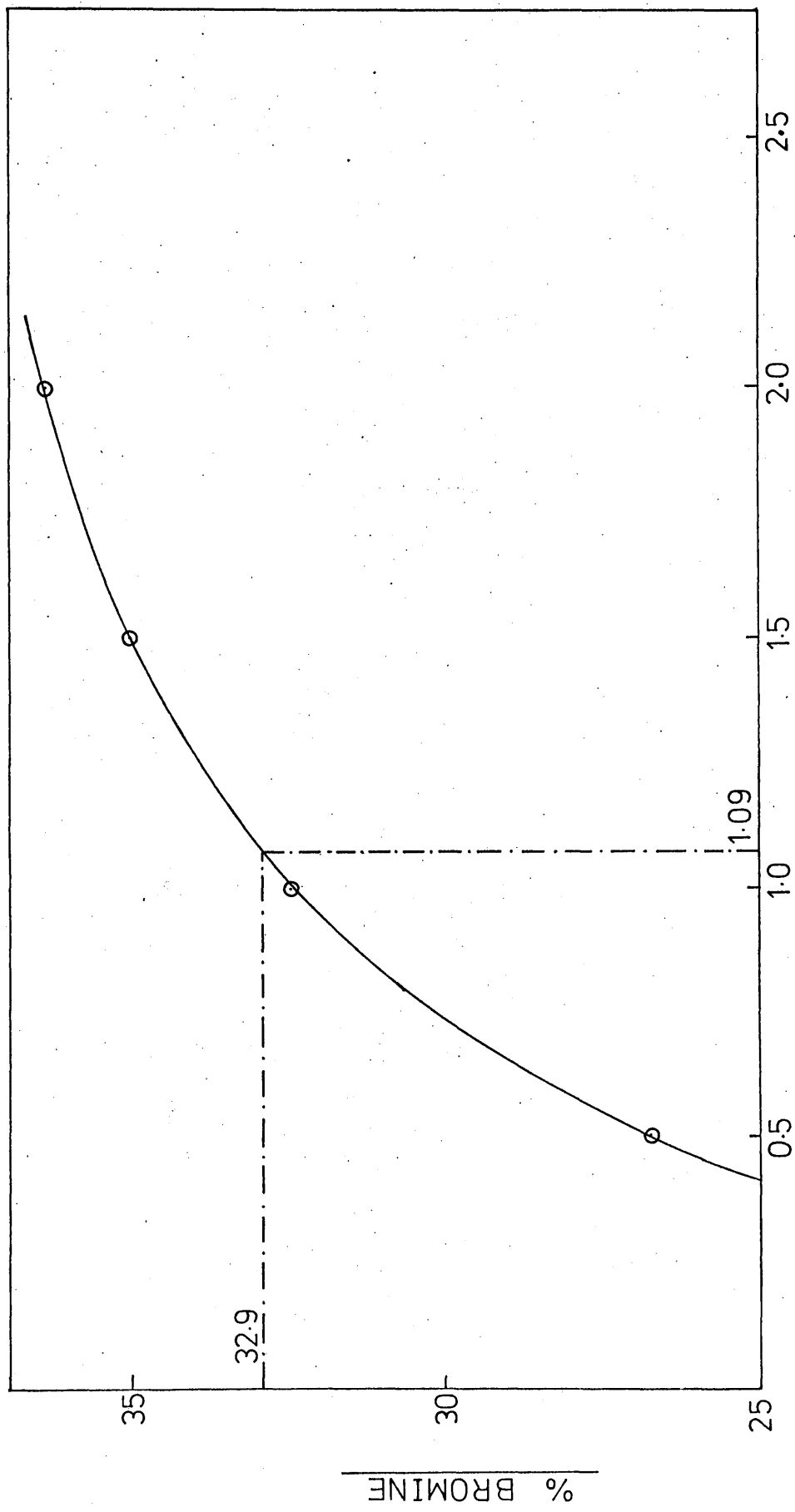


Figure 9.2 Graph of % BROMINE content in copolymer vs. theoretical copolymer 2BEM:AN monomer ratios.

for the AN/2BEM system are similar to those for the 2CEM/AN monomer pair.

The copolymer was a white powder, readily soluble in acetone.

9.4 THERMAL ANALYSIS

(i) Thermogravimetry

The weight-loss curve obtained from the programmed degradation of 5mgs of copolymer D is shown in Figure 9.3. Two distinct regions of weight-loss are clearly discernable. The first stage begins at approximately 275°C, reaches a maximum rate of volatilisation at 307°C and accounts for 35% of the original sample weight.

The second stage involves a more gradual volatilisation process which reaches a maximum rate in the region of 400°C and accounts for a further 40% of the sample weight at 500°C. This weight-loss profile was found to be reproducible over a number of experiments.

(ii) Differential Thermal Analysis and Differential Scanning Calorimetry

The DSC and DTA curves for copolymer 2-BEM/AN which are shown in figure 9.4 afforded similar information. The outstanding feature of both curves is the broad exotherm which peaks at approximately 300°C. The low temperature peak at 75°C is attributed to the glass transition, Tg. The two curves show anomalous behaviour at temperatures above 350°C.

The DTA trace (curve II) exhibits a marked discontinuity at 350°C which is reproducible over a number of experiments, and may be due to a physical change in the polymer sample as it is heated. In order to determine the exact nature of this

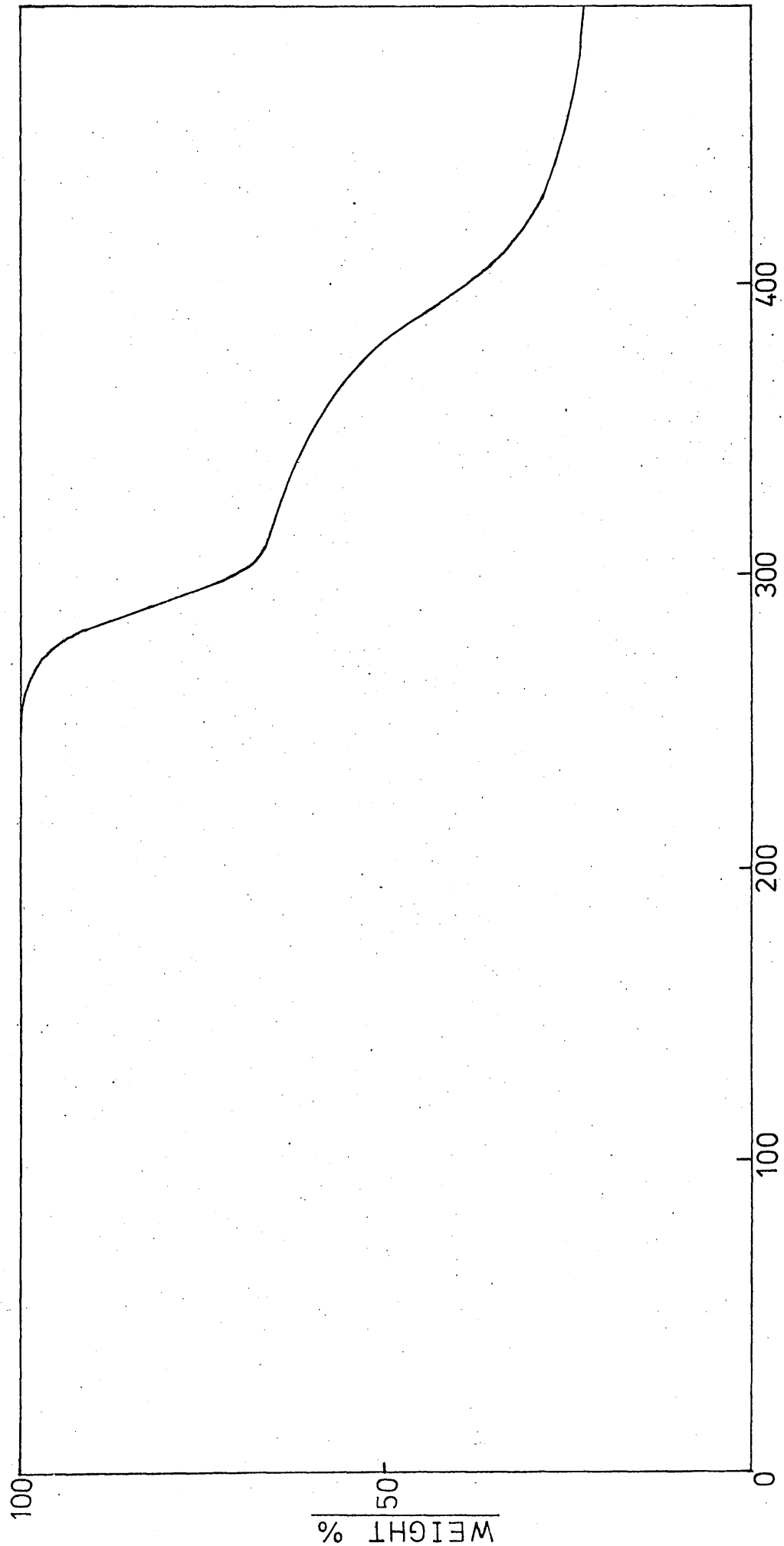


Figure 9.3 TG curve for 5 mg of copolymer 2BEM-AN.

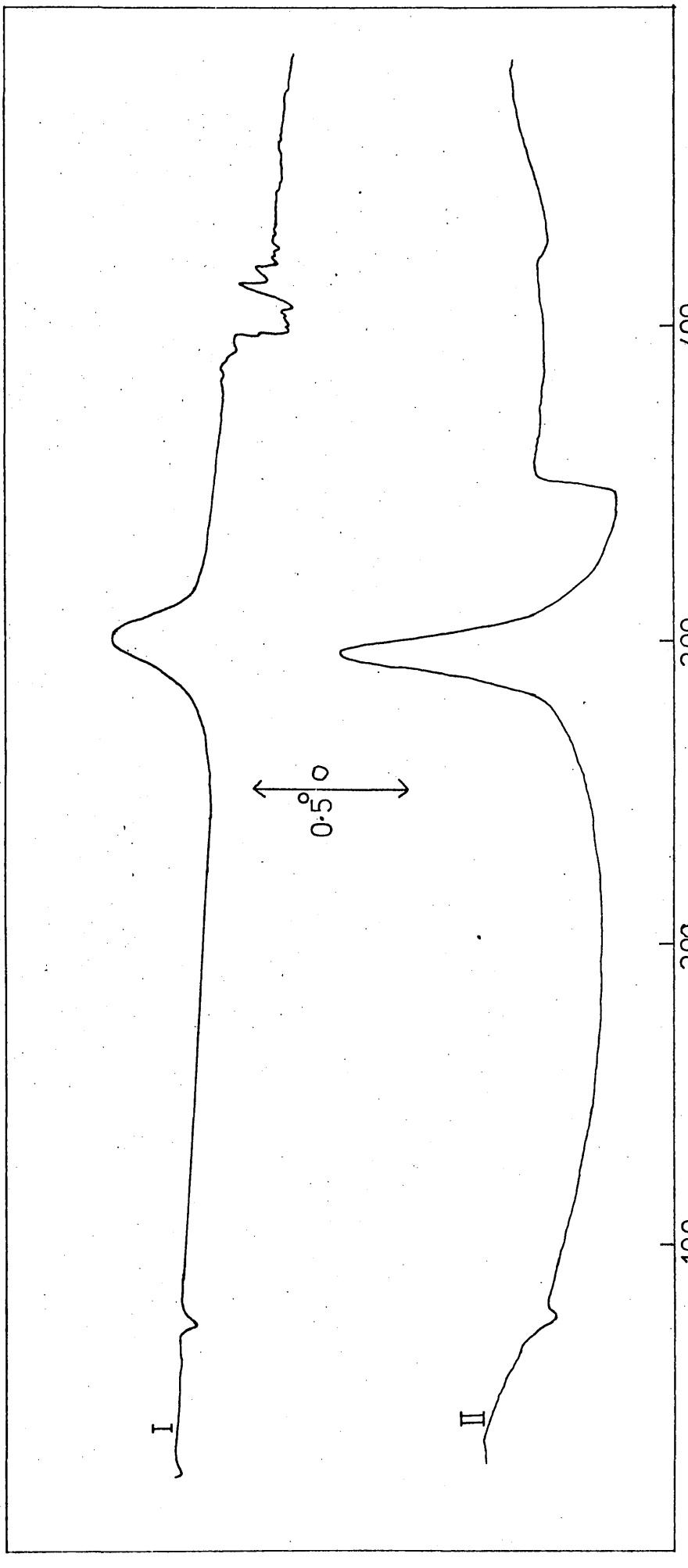


Figure 9.4 I - DSC profiles of 5 mgs copolymer 2BEM-AN 10°/min. II - DTA profile 8.7 mg copolymer 2BEM-AN 10°/min. (reference - glass beads)

change, 5mgs of powdered copolymer sample was heated through the exothermic reaction to 320°C and then allowed to cool. The heated sample was observed to be a dark brown powder. It was then re-heated to 375°C and inspection showed that intumescence had occurred. As the sample foamed and swelled due to the evolution of gases, the thermocouple which records the sample temperature was displaced causing the discontinuity in the DTA curve.

This intumescence also accounts for the rather shallow and irregular endotherm at 400°C observed in the corresponding DSC curve (I). The heat of the reaction ($-\triangle H$) for the exothermic process was obtained from the area under the DSC curve using the equation shown in Chapter 2. It was found to be 4kcal/mole of acrylonitrile presuming that the co-monomer does not contribute to the exothermicity. This value is lower than in acrylonitrile itself[118] and suggests that the oligomerisation reaction is being retarded to some extent.

(iii) Thermal Volatilisation Analysis

Figure 9.5 illustrates a typical TVA curve obtained from a programmed degradation to 500°C of a 50mg powdered sample of copolymer 2BEM/AN. Two distinct stages of volatilisation are discernable. Evolution of condensables volatile at normal temperatures begins at 260°C, reaches a maximum rate of volatilisation (Tmax) at 303°C and ends around 350°C. The second stage consists of a much broader peak which attains a maximum volatilisation rate (T́max) at 410°C, and continues as a high plateau at 500°C.

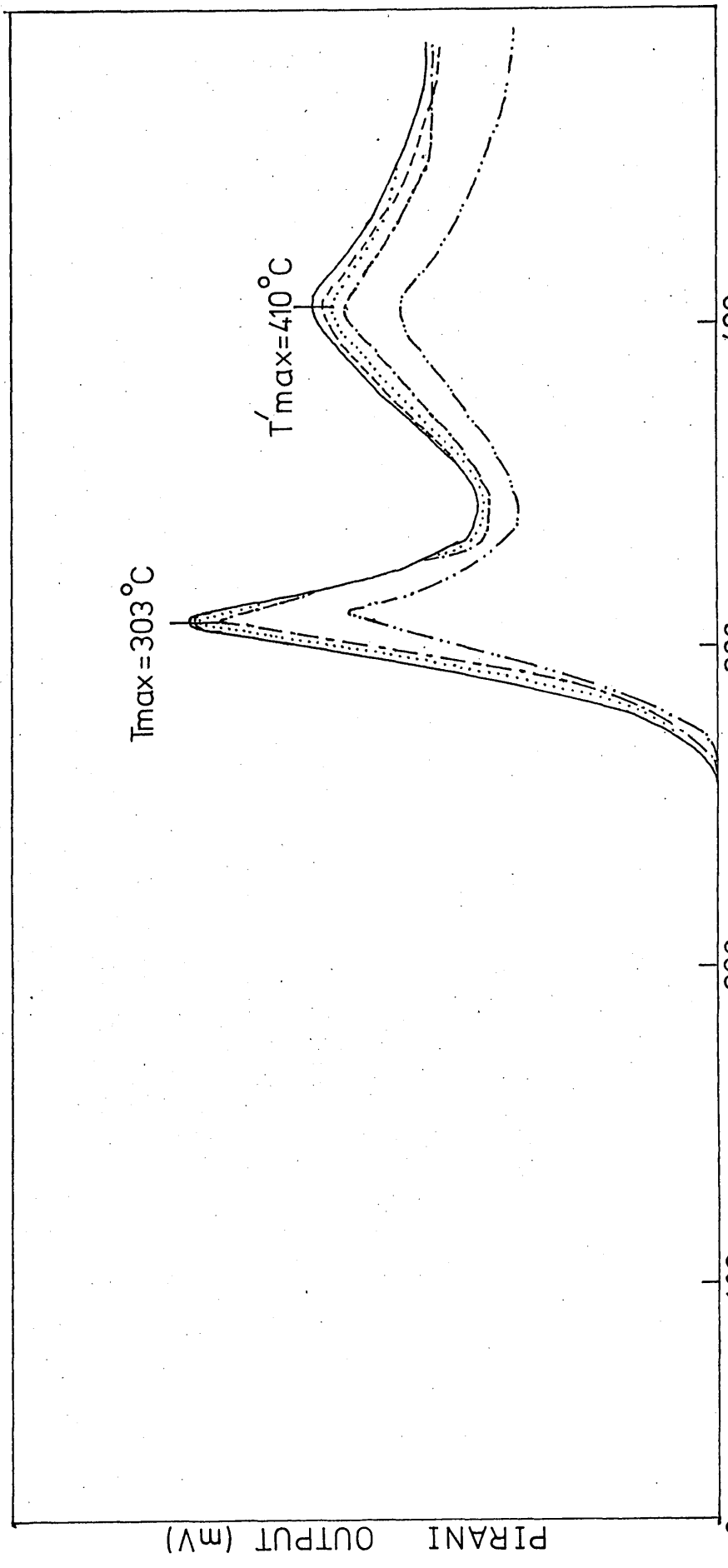


Figure 9.5 TVA of 50 mg copolymer 2BEM-AN heated at 10°C/min.

The $0^{o}C$, $-45^{o}C$, $-75^{o}C$ and $-100^{o}C$ traces are virtually co-incident throughout the entire temperature programme. They are however, separated from the $-196^{o}C$ trace which mirrors the general volatilisation profile.

The behaviour of the traces from the four parallel traps indicates that the condensables which are being evolved in each stage of the degradation are highly volatile at ambient temperatures, and that they can be trapped only at liquid nitrogen temperatures under normal TVA conditions. This evidence therefore, suggests that 2BEM monomer is not produced from this copolymer system.

The $-196^{o}C$ trace also indicates that non-condensable species are being formed concurrently with the condensable fraction during the initial stages of degradation. PAN itself does not begin to release non-condensables until temperatures in excess of $350^{o}C$, while P2BEM homopolymer gives exclusively monomer. The appearance of these non-condensable products at such low temperatures suggests therefore, that one of the first degradation reactions to occur involves interaction between the respective co-monomers.

After each TVA experiment a substantial deep yellow coloured 'cold ring' fraction was observed at the top of the degradation tube. Although insoluble in carbon tetrachloride it was analysed by infra-red spectroscopy as a solution in chloroform.

A black intumescent residue remained on the bottom of the degradation tube after programmed degradation to $500^{o}C$. This was examined by infra-red spectroscopy in the form of a

KBr disc.

It is evident from the results of thermal analysis that the degradation of the copolymer 2BEM/AN occurs in two distinct stages. In order to achieve a better understanding of the overall mechanism of thermal decomposition, it is therefore, clearly of primary importance to characterise the features and products evolved in each stage of degradation. To this end a series of dynamic degradations to 325°C were carried out, in addition to isothermal heating programmes at selected temperatures. The various fractions from these degradations were subsequently analysed by standard analytical methods. The features and degradation products of the second stage were investigated by heating the residues which remained after the initial programmes at 10°/min to 500°C.

9.5 PRODUCT ANALYSIS

(i) First Stage

Figure 9.6 shows a typical sub-ambient TVA trace of the condensable products formed after dynamic degradation of 26 mgs of copolymer D to 310°C at 10°C/min.

The products which give rise to the various peaks in the distillation system are presented in Table 9.1.

Table 9.1 Volatiles Identified from Sub-ambient TVA Trace Illustrated in Figure 9.6

Peak Number	Products Identified
1	Ethylene
2	Carbon Dioxide
3	Vinyl Bromide, Hydrogen Bromide (minor) Hydrogen Cyanide (minor)
4	Acetaldehyde, 1,2 Dibromoethane

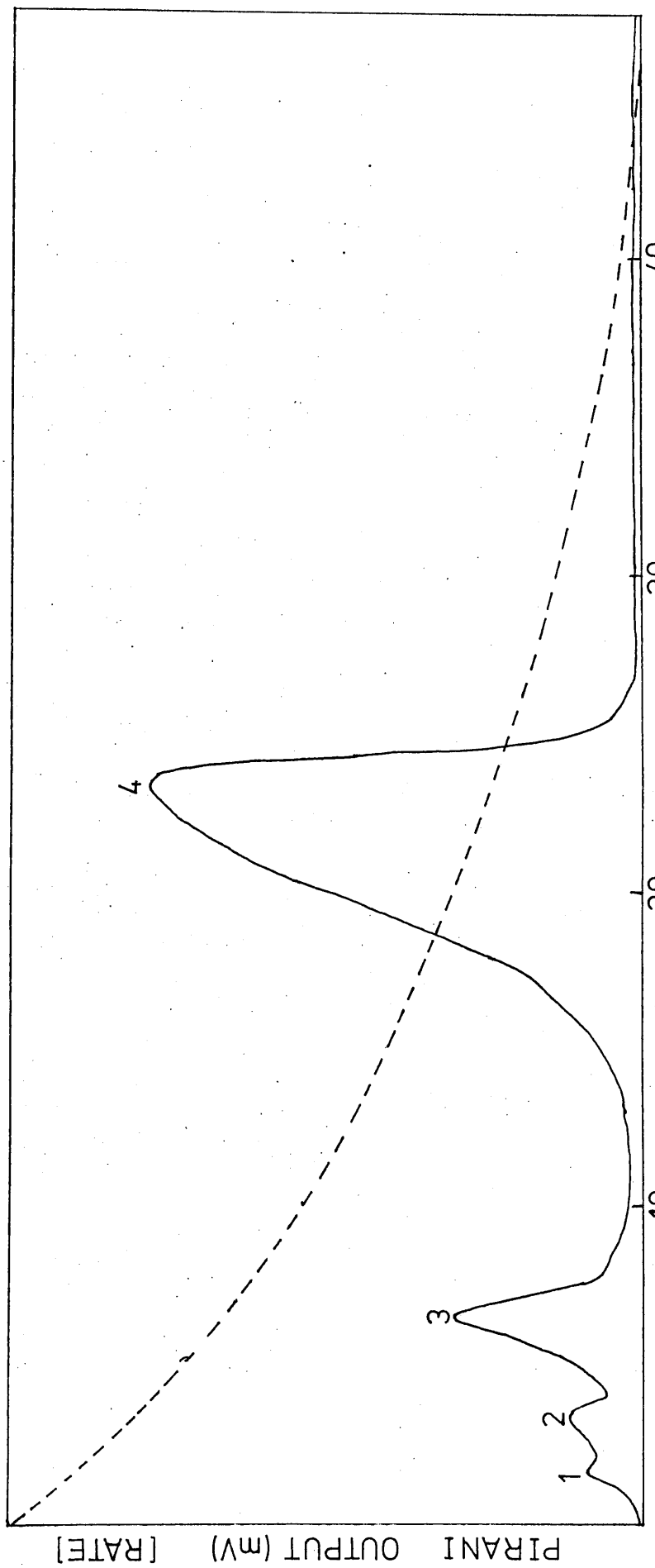


Figure 9.6 SUB-AMBIENT TVA trace of 26 mgs of copolymer 2BEM-AN degraded dynamically at 10°C/min. t 310°C.

The information in Table 9.1 confirms the absence of 2BEM monomer among the degradation products as indicated by TVA. Acetaldehyde and 1,2 dibromoethane are the major products from this first stage although vinyl bromide is formed in appreciable quantities. Ethylene, carbon dioxide, HBr and HCN are minor products. No ammonia was detected from this first stage of degradation.

The major condensable products from this initial volatilisation stage are not found among the decomposition products of either homopolymer and must therefore be associated with an interaction of the comonomer units during the exothermic reaction.

The non-condensable products which are released during this volatilisation process were identified as being mainly methane with traces of carbon monoxide. No hydrogen was detected at these temperatures.

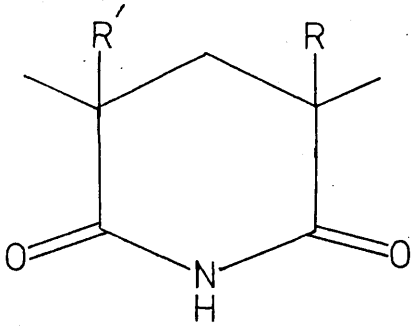
It was also observed that no 'cold ring' fraction was formed after this initial degradation step. This contrasts with the behaviourof PAN homopolymer in which chain fragments are produced as a consequence of the exothermic nitrile oligomerisation process.

The structural changes which take place in the copolymer during the first stage of degradation were examined by infrared spectrsocopy. Figure 9.7 shows the spectrum of the undegraded polymer in the form of a KBr disc and the spectrum obtained after the copolymer had been thermally degraded to $325^{0}C$. The first point to note is the relative decrease in

Figure 9.7 INFRA-RED SPECTRA of (I) undegraded copolymer (KBr disc) (II) copolymer degraded to 325°C (KBr disc).

the nitrile absorption at 2238cm^{-1} in spectrum II. Although greatly diminished, this absorption indicates that unreacted nitrile groups are present in the polymer chain after the first stage of degradation has taken place. The relative reduction of the nitrile absorption indicates that the majority of these groups have been chemically modified during the exothermic reaction.

The carbonyl absorption region is substantially altered in the degraded sample. The original carbonyl peak at 1730cm^{-1} is greatly reduced in intensity and forms part of a broad absorption in the region 1680-1735cm^{-1}. A new carbonyl peak however, is observable at 1695cm^{-1} which may be associated with a cyclic imide structure:-



Carbonyl absorption in cyclic imides eg glutarimide[74,119] occurs close to 1700cm^{-1} and this is true for many other cyclic imides.[120] The shoulders which occur at 1805 and 1765cm^{-1} are indicative of anhydride type structures.

The pyrolyzed sample also shows new peaks at 1630 and 1550cm^{-1} which have been ascribed to conjugated nitrile sequences,[121] but may also include N-H modes. The fingerprint region in spectrum II shows a general decrease in the intensity of the various absorptions although a new peak appears at 1020cm^{-1}. This is

thought to be associated with the anhydride type absorptions which occur in the carbonyl region.

The first stage of thermal degradation is therefore characterised by an exothermic reaction in which 35% of the original weight is lost in the form of small volatile products, the major proportion of which consists of acetaldehyde and 1,2 dibromoethane. Methane and carbon monoxide are also evolved during this reaction although no hydrogen, ammonia or chain fragments were detected.

The polymer undergoes a number of structural changes which involve the interaction of the pendant nitrile and ester groups of the comonomers to form cyclic imine and imide structures.

(ii) Second Stage

The sub-ambient TVA curve of the condensable volatiles produced from the second stage of the decomposition of copolymer 2BEM/AN is shown in Figure 9.8, and the identification of the respective peaks is presented in Table 9.2.

Table 9.2 Volatiles Identified from Sub-ambient TVA Trace Illustrated in Figure 9.8

Peak Number	Products Identified
1	Propene
2	Isobutene
3	Carbon Dioxide
4	Hydrogen Cyanide & Acetaldehyde (minor)
5	Isocyanic Acid (HNCO)
6	Isocyanic Acid & Methacrylonitrile (minor) & 1,2 Dibromoethane (minor)

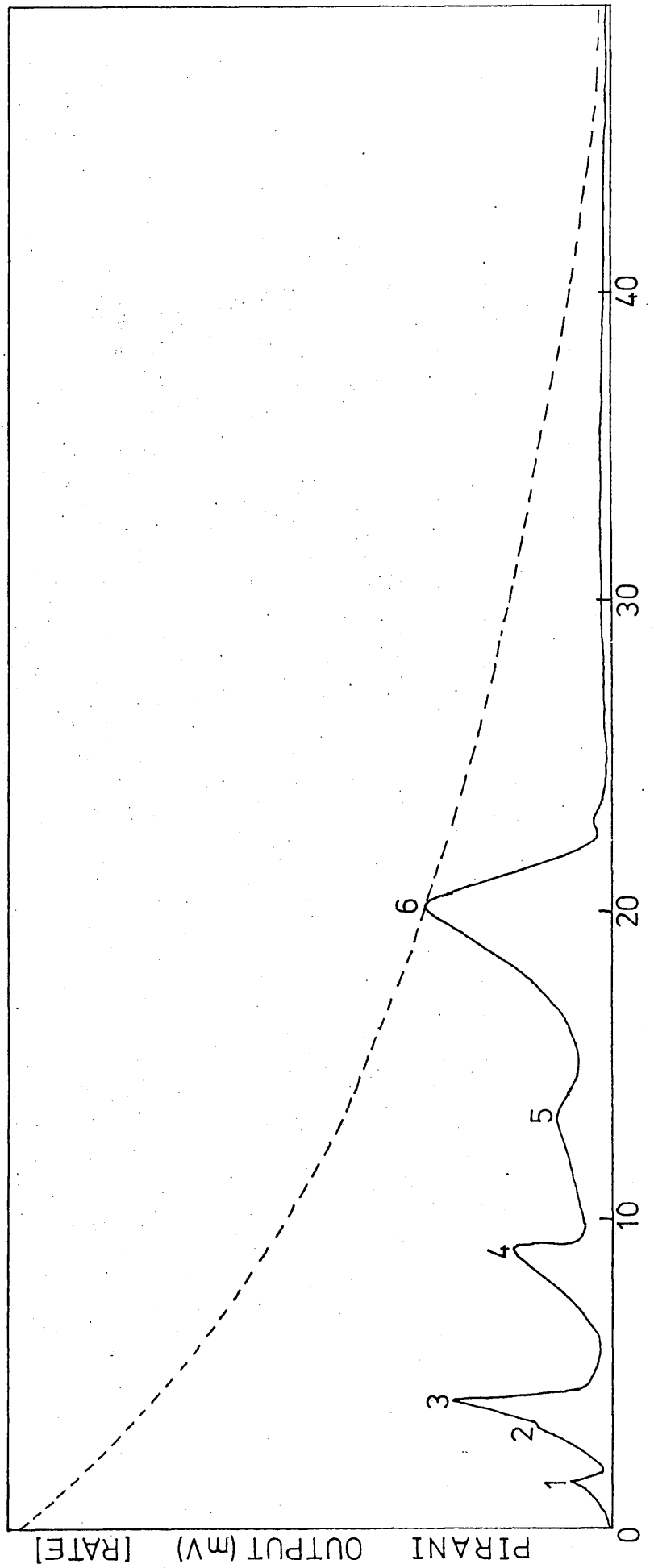


Figure 9.8 SUB-AMBIENT TVA trace of condensable products from residue of 25.5 mg of copolymer 2BEM-AN heated isothermally at 285°C for 1 hour then heated to 500°C at 10°/min.

Figure 9.8 again shows the absence of high boiling species among the degradation products. Isocyanic acid, hydrogen cyanide and carbon dioxide are found to be the major condensable products formed in the second stage of the copolymer degradation. Acetaldehyde and 1,2 dibromoethane which are found to be major decomposition products of the first stage are again observed in this secondary reaction, although to a much smaller extent. Minor amounts of propene, isobutene and methacrylonitrile were also detected. As in the first stage however, no trace of ammonia was found among the degradation condensables.

Carbon monoxide, methane and hydrogen were all present in the non-condensable gases evolved from this secondary decomposition process.

A substantial yellow coloured 'cold ring' fraction was formed on the upper part of the pyrolysis tube. Subsequent infra-red analysis gave the spectrum shown in Figure 9.9. The peak at 3370cm^{-1} is due to an imide N-H stretching mode.[121] Three strong absorptions are observed in the region 1600-1730cm^{-1}. The highest frequency absorption occurs at 1705cm^{-1} which is in the region normally associated with imide carbonyl absorption.[119,120] The lower frequency absorptions at 1660 and 1605cm^{-1} can be attributed to congugated imine structures but must also include N-H modes associated with the absorption at 3370cm^{-1}. The peaks at 2940 and 1455cm^{-1} are due to methylene vibrations and the absorption at 1380cm^{-1} may be attributed to a -C-N- stretching mode of the cyclic imide group which is known to occur in that

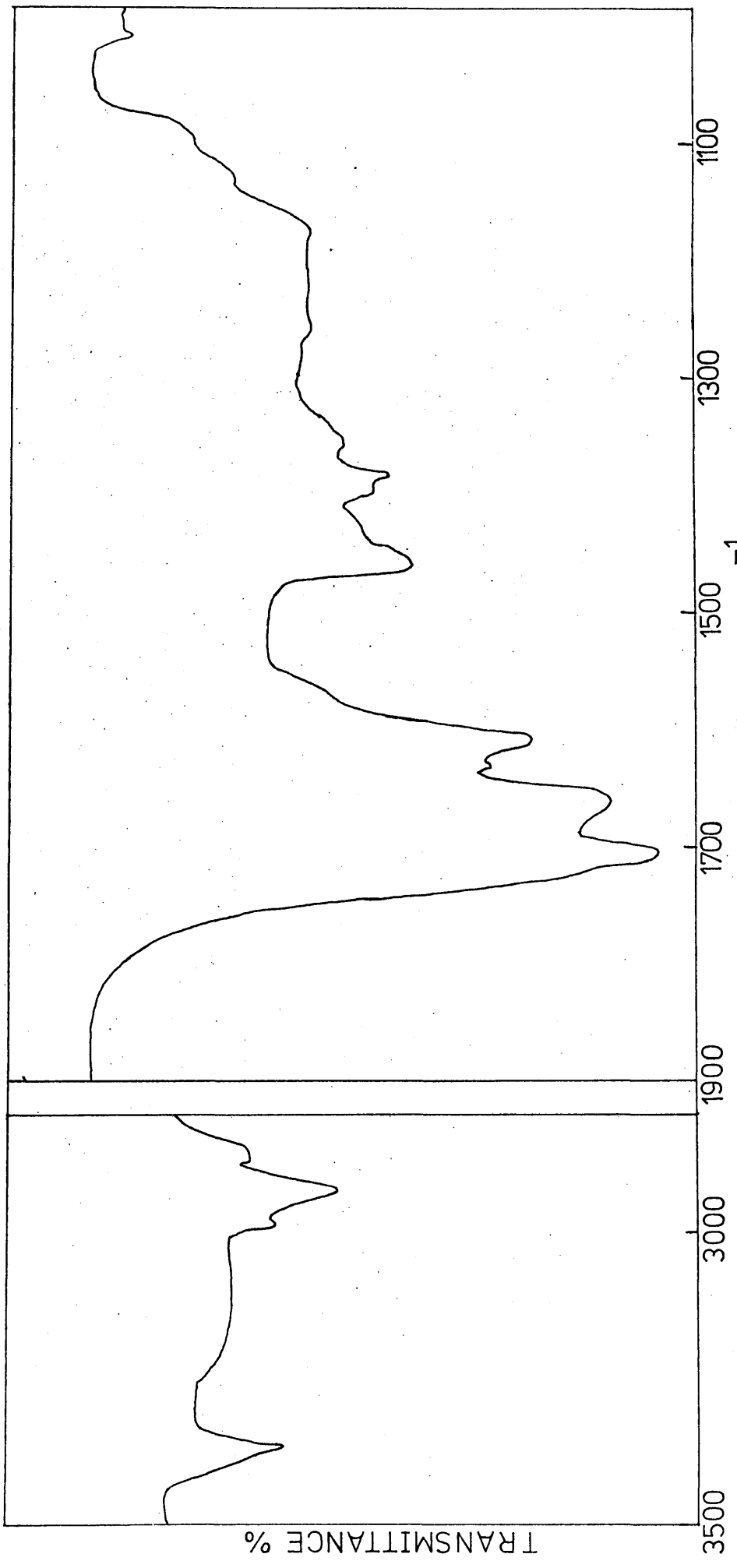


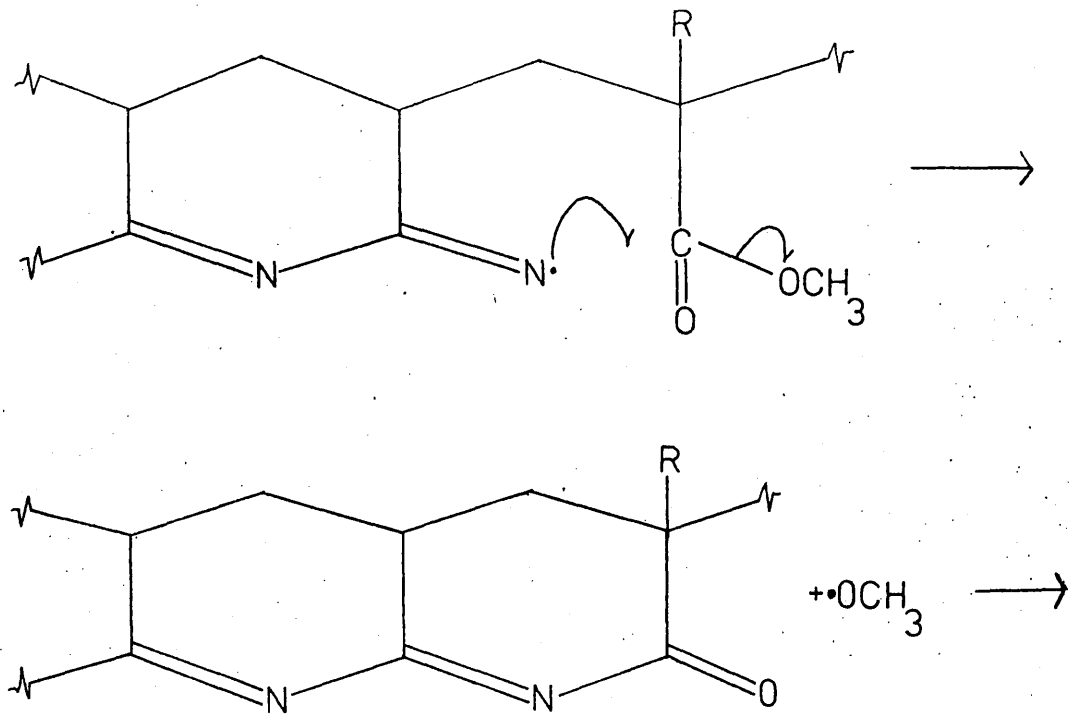
Figure 9.9 INFRA-RED SPECTRUM of CRF obtained from degradation of residue of 25.5 mgs copolymer 2BEM/AN preheated to 325°C for 1 hour then degraded to 500°C at 10°/min. ($CHCl_3$ solution).

region.[120]

From the chemical structure of the 'cold ring' and the nature of the condensable and non-condensable volatiles it seems that the second stage of degradation involves the breakdown of the cyclic imine and imide structures formed in the initial reaction. Chain scission, dehydrogenation and loss of HCN also take place at these higher temperatures.

9.6 DISCUSSION

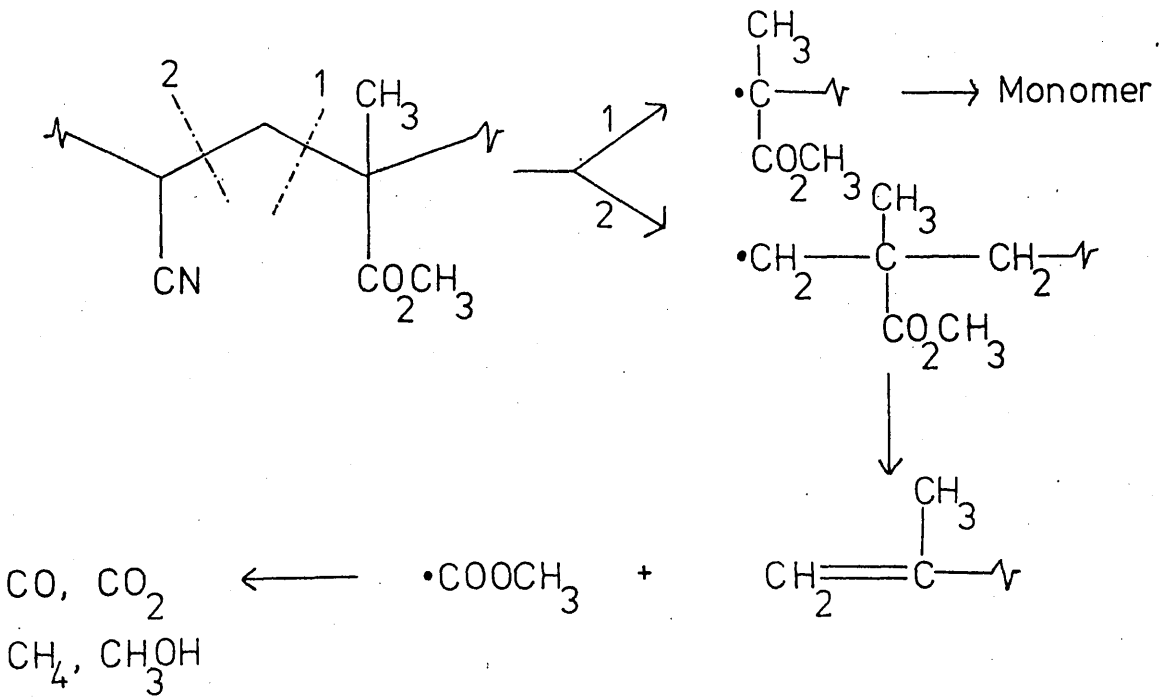
From the evidence it is clear that two separate reactions take place in the decomposition of the 2BEM/AN copolymer, namely, (a) intramolecular cyclisation of the pendant nitrile and ester groups with concurrent displacement of small volatile species and (b) the thermal breakdown of these secondary structures alongwith chain scission and dehydrogenation. Grassie and McGuchan[96] have examined the effect of various amounts of MMA, MA and benzyl acrylate comonomers on the thermal degradation of PAN. They found that as the amount of comonomer increased the intensity of the exotherm decreased and broadened. Methane, carbon monoxide, carbon dioxide and methanol appeared among the volatile products of MA and MMA copolymers in addition to ammonia and hydrogen cyanide. The carbonyl band at 1740cm^{-1} in the infra-red spectrum disappeared and was replaced by a new carbonyl peak at 1670-1700cm^{-1}. From this evidence these investigators concluded that the oligomerisation reaction can by-pass the comonomer unit although this introduces a slow step into the mechanism which is manifested in a reduction and broadening of the exotherm.



CH_3OH + Polymer radical

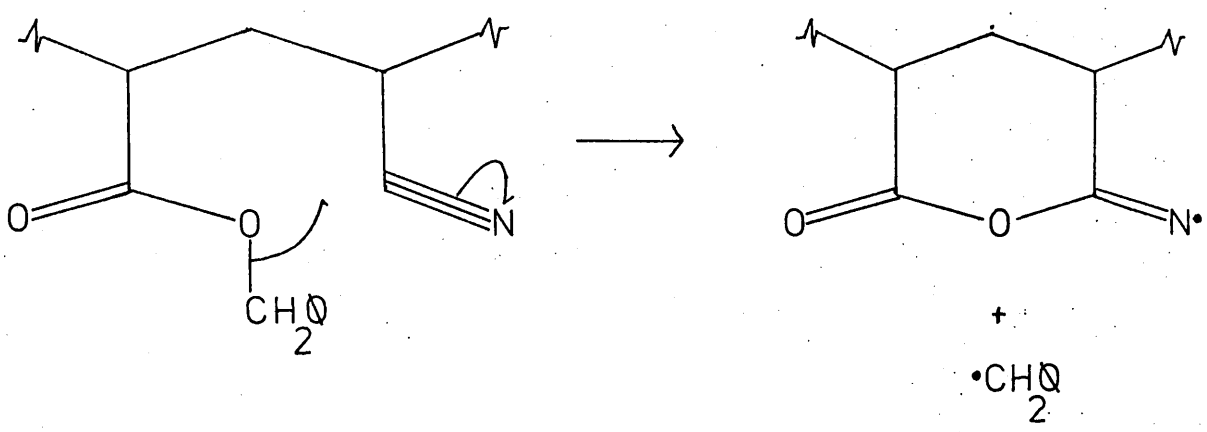
Hence, the comonomer terminates the cyclisation sequence but the kinetic chain is continued by hydrogen abstraction by the methoxy radical to produce a polymer radical which can re-initiate the oligomerisation reaction by a back-biting mechanism.

To explain the occurrence of methane and carbon monoxide they proposed the following reaction mechanisims derived from chain scission:-



The behaviour of benzyl acrylate copolymers differed from that of the MMA and MA systems in that toluene and not benzyl alcohol was found to be a major decomposition product.

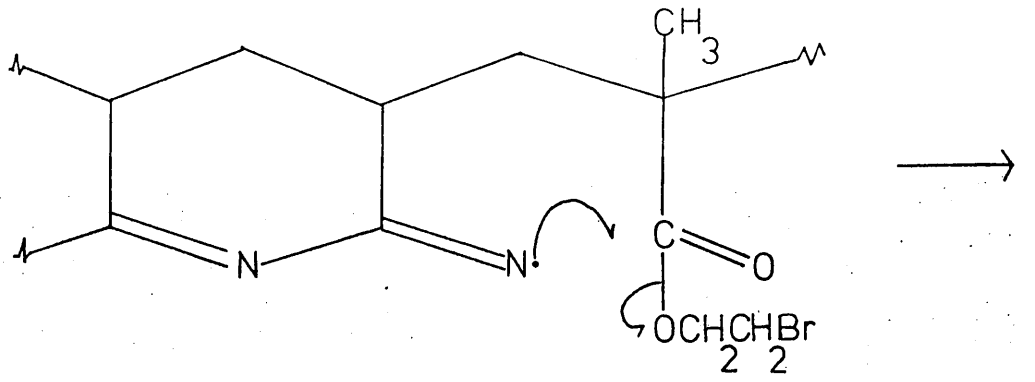
Grassie and McGuchan concluded that the BA unit may be involved in initiating the nitrile reaction rather than terminating it:-

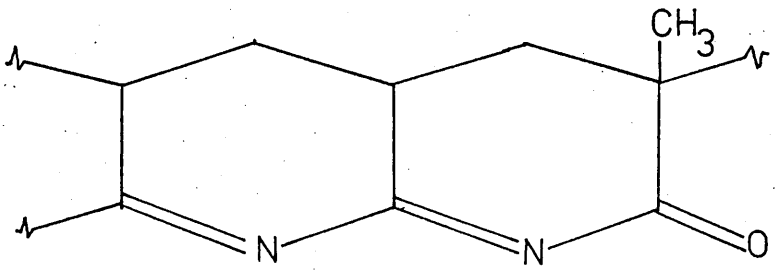


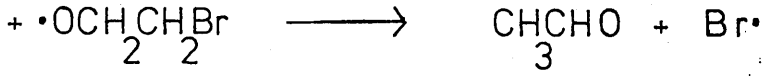
The removal of the bulky benzyl group may favour this reaction.

The occurrence of acetaldehyde and 1,2 dibromoethane early in the degradation of copolymer 2BEM/AN may be explained by reactions analogous to those outlined above.

It has been found in copolymers of 2BEM/MA (Chapter 7) that acetaldehyde is produced from the rearrangement of the 2-bromoethoxy radical through an ethylene oxide intermediate. In this copolymer system the 2-bromoethoxy radical would be produced from a termination reaction similar to that proposed for MMA/AN and MA/AN copolymers.

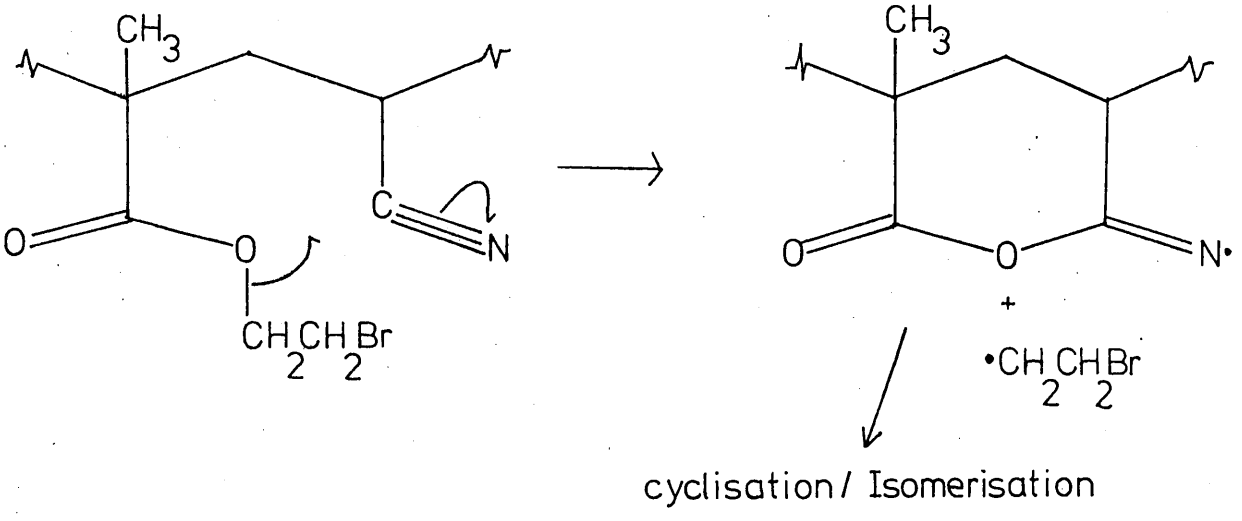




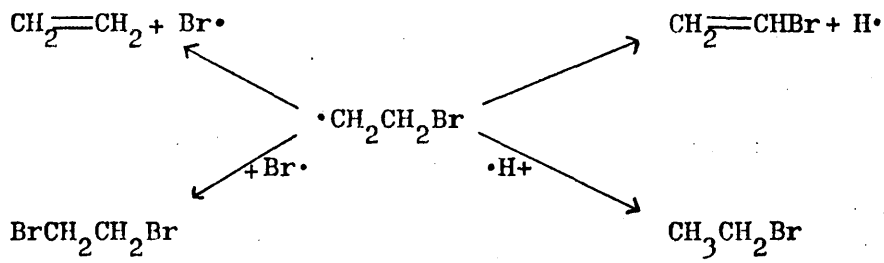


In this copolymer system however, the displaced alkoxy radical does not abstract a hydrogen to continue the cyclisation reaction, but isomerises to give acetaldehyde and a free bromine atom. This retardation may explain the low ΔH value for the exothermic reaction.

An initiation reaction analogous to that proposed for the BA copolymers can be envisaged for the 2BEM unit:-

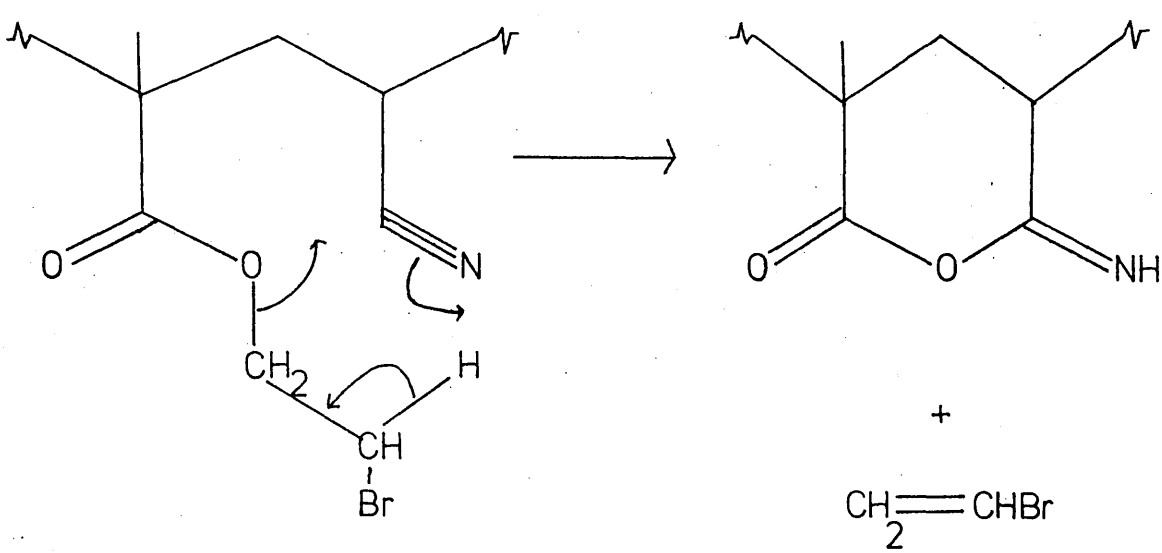


The isoimide structure formed can either proceed with cyclisation or isomerise to an imide group. There are also a number of possible reactions which the displaced bromoethyl radical can undergo:-



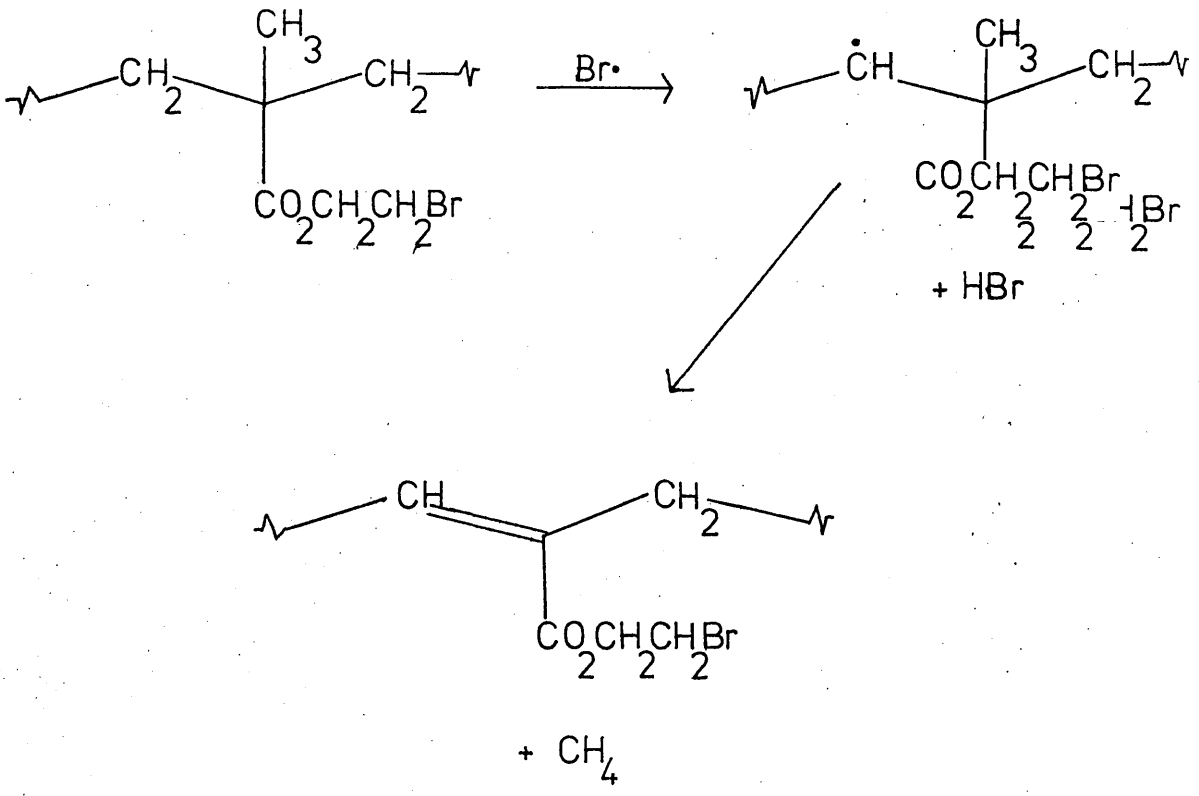
Hence, the bromoethyl radical can be a precursor for ethylene, vinyl bromide and 1,2 dibromoethane, which are all present among the decomposition products of the exothermic stage. The quantity of 1,2 dibromoethane suggests that the bromoethyl radical mainly undergoes a combination process with a free bromine atom which is released during the acetaldehyde isomerisation process. However, the production of ethylene and vinyl bromide supports the view that this bromoethyl radical exists and that it can react in a number of ways.

An alternative initiating reaction involves the production of vinyl bromide by a six-membered transition state:-



However this molecular mechanism does not allow for ethylene or 1,2 dibromoethane production and is therefore thought to be unlikely.

In contrast to MMA/AN copolymers studied by Grassie and McGuchan[96] the present system did not produce 2BEM monomer or chain fragments in the initial stages of pyrolysis. The absence of chain scission and depolymerisation reactions therefore, infers that methane formation must occur by an alternative route to that previously described. Such a process may involve the abstraction of a methylene proton with subsequent loss of a methyl radical. Although these methylene protons are considered relatively unreactive, the physical nature of the degrading polymer system may permit their removal.

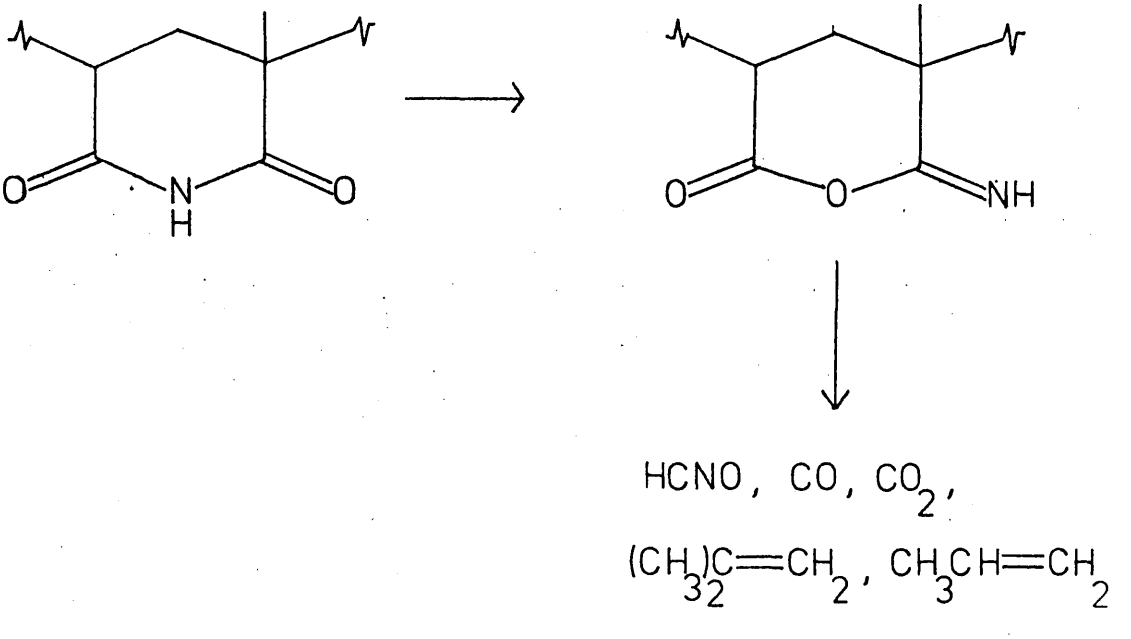


The hydrogen abstraction process may account for the small amount of HBr formed in the first stage. This main chain unsaturation will facilitate the loss of HCN from acrylonitrile groups accounting for the presence of this material at these higher temperatures.

These cyclic imine, imide and isoimide structures explain the shift of the carbonyl absorption to lower frequencies and the occurrence of anhydride type absorptions (isoimide). The extent of the weight loss indicates that there are few unreacted 2BEM units remaining after the exotherm has taken place. Spectral evidence suggests that this is also the case for acrylonitrile units.

At temperatures above 350°C these cyclic structures decompose to give isocyanic acid, carbon dioxide, carbon monoxide, isobutene and propene. Chain scission also takes place to give chain fragments and small amounts of methacrylonitrile. The unreacted AN units lose HCN as aromatisation takes place.

It has been established[122,123] that during amide pyrolysis the isoimide structure exists in equilibrium with the cyclic imide. These structures then break down to give the observed gaseous products:-



This mechanism receives support from recent work by McNeill and Zulfiqar[124] who studied the thermal decomposition of Ammonium Polymethacrylate. These workers identified imide structures at 280°C and found the same gaseous volatiles being evolved at higher temperatures.

It has also been suggested that HCN[111] is produced from the pyrolysis of these imide groups. However, it is thought that this product originates from isolated unreacted acrylonitrile groups which eliminate HCN at higher temperatures.

One interesting aspect of the thermal degradation of this copolymer system is the absence of ammonia from each stage of the degradation. This product is believed by Hay[116] to be formed in an elimination reaction which occurs at the terminal sites of the cyclic imine sequence in PAN homopolymer. In this 1:1 2BEM:AN copolymer however, the termination reaction occurs exclusively at 2BEM units giving rise to a conjugated keto-imine terminal structure, acetaldehyde and a free bromine atom. Hence, this evidence supports Hay's hypothesis.

Thus, all the evidence suggests that the 2BEM unit can participate in the nitrile oligomerisation reaction. The bulkiness of the ester side group can result in interaction and splitting-out of the bromoethyl radical or the ester group may terminate the cyclic sequence with elimination of an alkoxy radical. Chain scission and depolymerisation are less evident than might have been expected from the degradation characteristics of the parent methacrylate polymer and this is also consistent with the observed chemistry. The reduced importance of hydrogen

transfer processes is manifested in the reduction of the intensity of the exotherm. At elevated temperatures the secondary cyclic structures decompose to give small molecular gaseous products, alongwith chain scission and aromatisation.

CHAPTER 10

10.1 GENERAL CONCLUSIONS

The results of the present study may be summarised in the following way:-

(1) Poly(2-bromoethyl methacrylate) predominatly depolymerises to monomer in a manner essentially similar to PMMA. At higher temperatures there is evidence of trace amounts of products from ester decomposition.

(2) The reactivity ratios for the monomer pair 2BEM and MA were determined by an NMR spectroscopy method and found to be r_1(2BEM) = 2.77 ± 0.03 and r_2(MA) = 0.19 ± 0.02.

(3) The thermal stability of copolymers of 2BEM and MA is intermediate between those of the homopolymers. As the MA content of the copolymer is increased, depropagation is superseded by transfer processes which lead to a series of inter- and intramolecular displacement reactions involving an MA polymer radical and a 2BEM ester group. Such processes give rise to methyl bromide and 1,2 dibromoethane in the initial stages of degradation and acetaldehyde at higher temperatures.

(4) Acetaldehyde is formed from the rearrangement of a 2-

bromoethoxy radical through an ethylene oxide intermediate which decomposes at degradation temperatures.

(5) These displacement reactions also occur in the thermal degradation of 1:1 blends of P2BEM and PMA.

(6) In addition to depropagation, degrading styrene polymer radicals in a 1:1 copolymer of 2BEM and styrene can abstract either a hydrogen or bromine atom from the bromoalkyl group of a 2BEM unit.

(7) In a 1:1copolymer of 2BEM and acrylonitrile, 2BEM units can initiate or terminate the oligomerisation reaction of the nitrile groups, forming a series of cyclic structures which decompose at higher temperatures to produce a number of volatile gases.

10.2 SUGGESTIONS FOR FUTURE WORK

A study of the changes in molecular weight of 2BEM/MA copolymers at pre-volatilisation temperatures would yield valuable information on the nature of the initiation reaction in the decomposition of this copolymer system. Working at these lower temperatures would minimise the problem of insolubility.

A quantitative study of the gaseous volatiles evolved during the thermal degradation of 2BEM-styrene copolymers covering the entire composition range would determine the relative importance of hydrogen and halogen transfer reactions at any particular composition.

A similar quantitative study on the 2BEM-acrylonitrile copolymer system would reveal the relative importance of the

2BEM unit in initiation and termination of the nitrile oligomerisation reaction, which is relevant to the production of carbon-fibres.

The ultimate usefulness of halogenated polymers may depend on the stability of these materials under normal atmospheric conditions. To this end a parallel photochemical study of bromine containing copolymers would be vital.

A study of the relative flammability properties of the brominated homopolymers and copolymers could provide useful information relating the nature and amount of pyrolysis products to the burning characteristics of each system. The limiting oxygen index method devised by Fenimore and Martin[125,126] could provide such information.

APPENDIX 1

THE THERMAL DEGRADATION OF A 2BEM-MMA COPOLYMER

The polymerisation conditions used in the preparation of this approximately 1:1 copolymer are described in Chapter 2. Figure A1-1 shows the TVA curve obtained from heating 60mg of powdered polymer to 500°C at 10°C/min.

Complete volatilisation takes place by 450°C with no formation of non-condensable volatiles, a'cold ring' fraction or any residue. The TVA profile is indicative of the presence of high boiling products with the -75°C trace displaying a limiting rate effect which is characteristic of MMA monomer.[38]

Infra-red analysis of the volatiles confirmed that both monomers, 2BEM and MMA were indeed the sole pyrolisis products and hence it was concluded that they were formed by a depolymerisation mechanism, probably initiated at lower temperatures (i.e. 300°C) at unsaturated chain-end structures and at higher temperatures by random chain scission.

These results, therefore, suggested that no interaction takes place between the two monomer units during the copolymer decomposition.

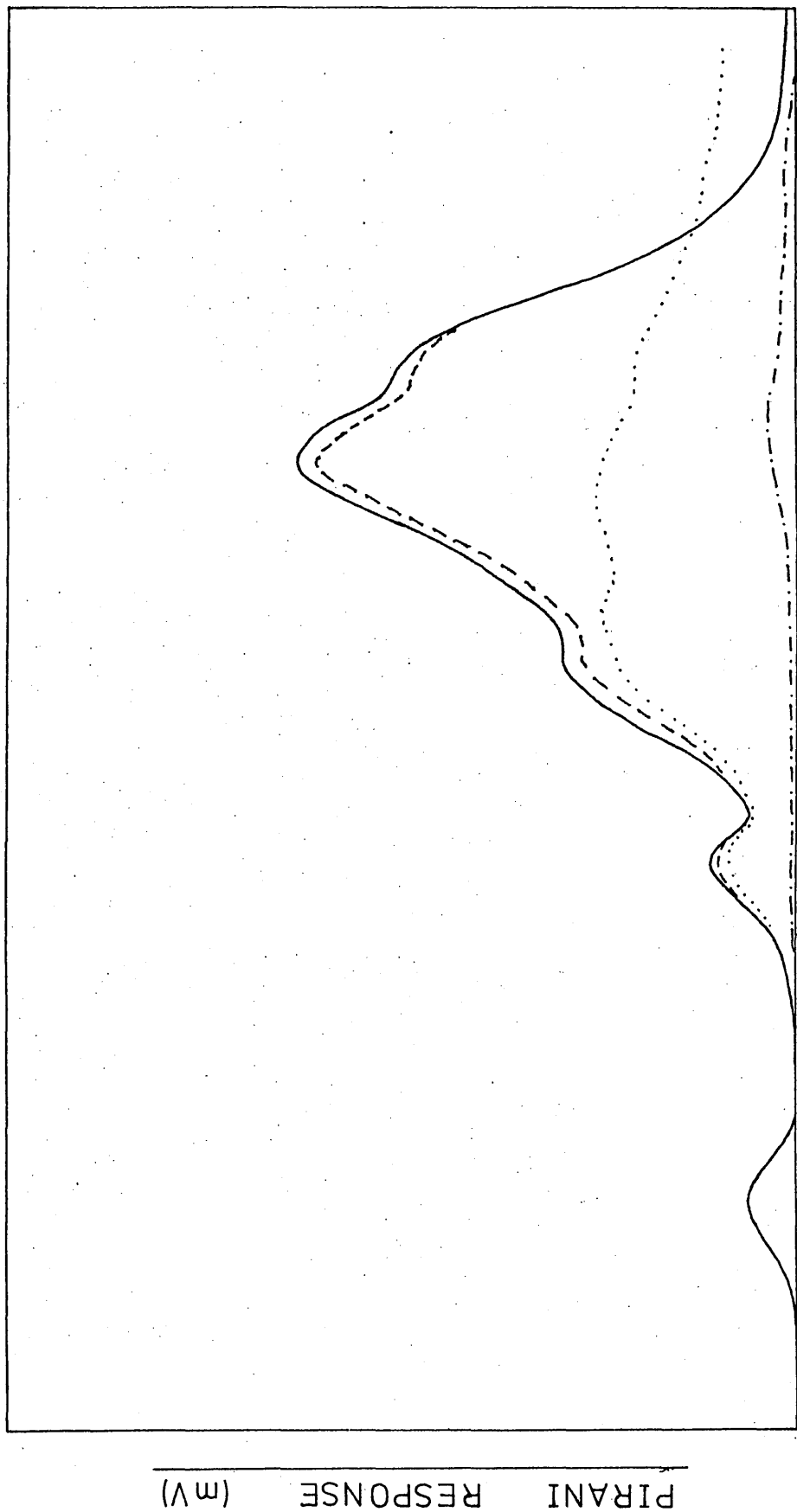


FIGURE A1-1 TVA THERMOGRAM OF COPOLYMER 2BEM-MMA, (60mg POWDER AT 10°C/min.).

APPENDIX 2

THE THERMAL DECOMPOSITION OF POLY(2-BROMOETHYL ACRYLATE)

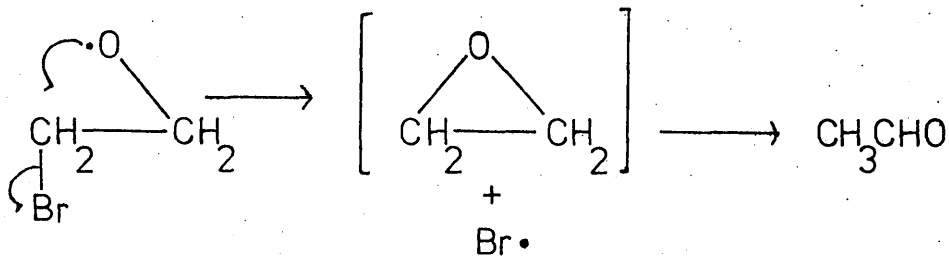
Monomer synthesis and polymerisation details are outlined in Chapter 2. A one stage volatilisation profile was obtained on programmed heating of 40mg of polymer at $10^{o}C$/min to $500^{o}C$, with a maximum rate occurring at $\sim 400^{o}C$. However, the main fraction of degradation, constituting approximately 60% of the original polymer weight, was condensed on the upper part of the degradation tube. Analysis of this coloured fraction indicated the presence of back-bone unsaturation, carbon-bromine bonds and cyclic ketone structures, which suggested that it was essentially modified chain fragments. Very little residue remained on heating to $500^{o}C$.

The volatile products identified by the normal spectroscopic techniques were found to consist mainly of acetaldehyde and carbon dioxide with minor amounts of hydrogen bromide short chain fragments with traces of bromine. Non-condensable gases were also formed although no 2-bromoethanol was detected. Acetaldehyde was measured quantitatively by gas-liquid chromatography as described in Chapter 2 using n-butanol as reference and found to account for 23% of the original polymer weight.

Grassie et al[18] have shown that poly(n-alkyl acrylates) thermally decompose to produce the corresponding alkyl alcohol and carbon dioxide as the major condensable volatiles. The fact that P2BEA produces acetaldehyde rather than the expected 2-bromoethanol may be most satisfactorily explained in the

following way assuming that the manner of decomposition is the same for both cases.

The 2-bromoethoxy radical, which is formed during degradation, does not merely abstract a hydrogen atom but eliminates a bromine atom to produce ethylene oxide in the following manner:-



This ethylene oxide intermediate is unstable at degradation temperatures and further rearrangement takes place to give acetaldehyde. The presence of hydrogen bromide among the volatiles is further evidence for the formation of free bromine atoms.

It was concluded from these results that the decomposition of P2BEA was similar to other acrylate systems except that the brominated ethoxy radical formed during pyrolysis rearranges to produce a free bromine atom and ultimately acetaldehyde rather than hydrogen abstraction to form the corresponding alcohol.

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